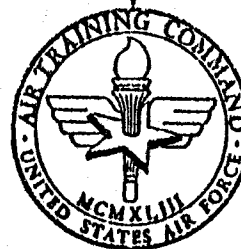DEPARTMENT OF WEAPONS TRAINING
LOWRY AIR FORCE BASE
COLORADO

T R A N S I S T O R S

IN SERVICE TRAINING COURSE

CHAPTER 2

CONDUCTION IN SOLIDS

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CHAPTER 2
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CONDUCTION IN SOLIDS

Abstract - The chemical behavior of the elements is related to the
structure of the atom. Chemical reactions are discussed to introduce
the covalent bond. The electronic structure of semiconductor crystals
is analyzed to show the origin of both hole and electron current
carriers. The temperature sensitivity of semiconductors is explained
by considering thermal agitation. The mechanisms of conduction in
semiconductors, both drift and diffusion, are given considerable
attention. Finally, the important physical properties of many
semiconductor materials are evaluated.

GENERAL

Now that the fundamental concepts of the diode and the transistor have been introduced, a more exact explanation of conduction in solids will be attempted. From this wil follow a discussion of semiconductor devices on a more exact basis.

Confusion often results when semiconductors are explained assuming the existence of holes and electrons then treating them as free particles unless certain restrictions are clearly understood. The operation of vacuum tubes can be adequately explained by considering the action of individual free particles, such as electrons and ions, because the separation of these charged particles is great enough that the interactions between them can be neglected. However, this is not the case when solid state devices are to be explained. The entire structure of the solid must be investigated as there are interactions between the mobile current carriers and the closely packed immobile atoms. For this reason, a certain amount of the physics and chemistry of solids must be discussed before an intelligent view of semiconductors can be had.

STRUCTURE OF THE ATOM

In the ensuing discussion it is assumed that the reader has a fundamental knowledge of atomic physics. The explanation of the atom will be conducted as a review. Only those points necessary for an understanding of solid state phenomenon will be covered in detail.

The atom can be thought of as a positively charged nucleus surrounded by a cloud of negatively charged electrons. The nucleus is composed of protons having a unit positive charge and neutrons having no charge. These two nuclear particles make up the major portion of the atomic mass. The electrons have a unit negative charge so an neutral atom has an equal number of protons and electrons. The electrons are extremely small particles and contribute little to the total atomic mass.

The negative electrons can be pictured as existing in orbits around the nucleus. These orbits are not random, but are arranged in some definite manner. Figure 2.1 illustrates this point with a diagrammatic representation of the first 20 elements on the periodic chart. Circular orbits are indicated at definite distances from the nucleus. This is not actually the case; the given orbits are meant to indicate that the electron possesses a certain energy (kinetic energy from its motion and potential energy from its proximity to the nucleus). The position of the electron is uncertain, but it can be thought to describe a three dimensional elliptical orbit (ellipsoidal shell). The energy is somehow related to the mean diameter of the orbit so, although it is not exactly correct, the orbit will be considered circular. This is done to simplify analysis, but it should be remembered that a large diameter orbit indicates a high energy electron, and only approximates the actual path of the particle.
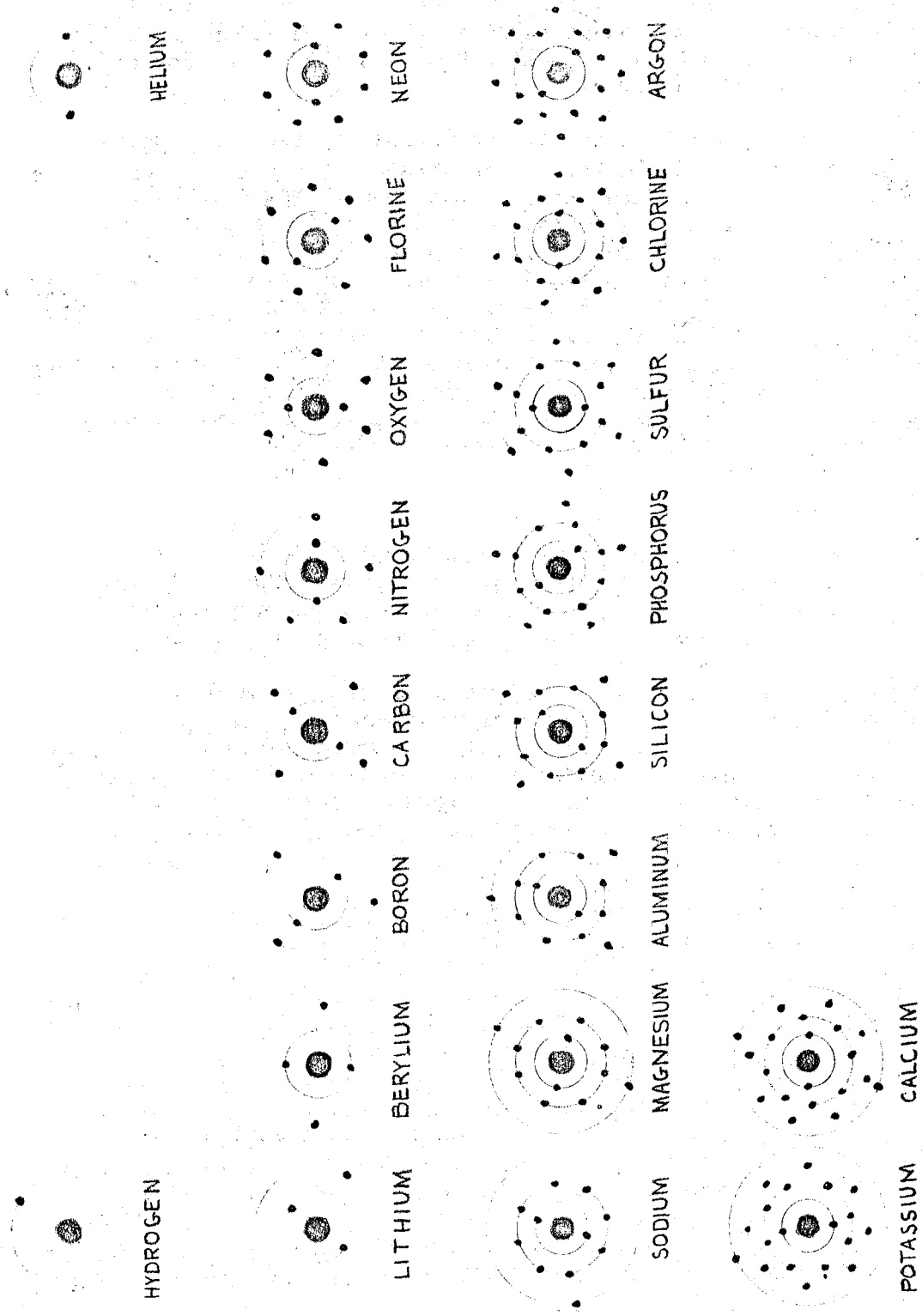
Figure 2.1. Electron Shell Configurations for the First Twenty Elements on the Periodic Chart.

The simplest element is hydrogen with a single electron in orbit about a proton nucleus. The next element, helium, has a nucleus, containing two protons and two neutrons, which shows a double positive charge. Two electrons orbit at equal distance from the nucleus.

The third element, lithium, has a nucleus with a charge of -3. There are three electrons circling the nucleus, but the third electron has assumed another larger diameter orbit. Continuing through the elements from lithium to neon, electrons are added in this second orbital path, or shell. However, with the sodium atom, a third shell is started.

CHEMICAL REACTIONS

It appears that these electron shells can only hold a certain number of electrons. Once these shells are filled, a new one is started. The filling of these electron shells and the behavior of partially filled shells is of particular interest because the difference in the chemical properties of different elements can be atributed, in part, to the arrangement of electrons in the outer shell.

Formation of Ions. Elemental lithium will react with florine gas to to form solid lithium floride. In this reaction, an electron is transfered from the outer shell of the lithium atom to the outer shell of the florine atom, as shown in figure 2.2a. The lithium atom is now lacking one electron so it will exhibit an overall charge of -1, while the florine atom will have a net charge of -1.
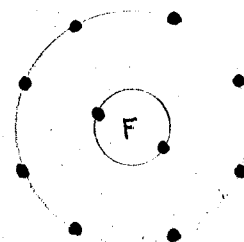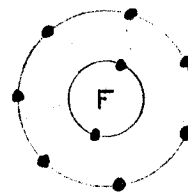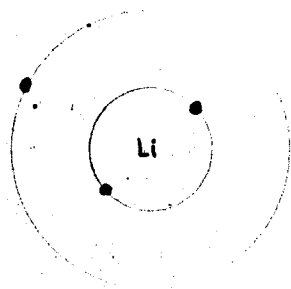
The fact that lithium will give up an electron to florine can be related to the configuration of its outer electron shell. In the lithium atom, the single electron in the second shell is shielded from the -3 charge of the nucleus by the two electrons in the first shell. Hence, this electron will be loosely bound to the nucleus and can easily be removed. However, in the florine atom, the two electrons in the first shell do not effectively shield the -9 charge of the nucleus so the 7 outer shell electrons are held by an appreciable portion of the nuclear charge. There is room for another electron in this second shell (to a maximum of 8) so, if an extra electron is available, it can go into the second shell where the electrons are far enough apart that the nuclear attraction for any electron in the shell is considerably greater than the mutual repulsion between them. This explanation accounts for the tendency of flourine to form a negative ion.

The reaction between berylium and oxygen, forming berylium oxide, supports this concept. Berylium will loose two electrons to oxygen as indicated in figure 2.2b. The reason that it looses these electrons is the same as that given for lithium, but this tendency is not so pronounced. The higher positive charge of the nucleus exerts a stronger influence on the second-shell electrons through the first shell. Berylium will generally loose both electrons because the attractive force on the second electron is not increased after the first is removed. The attraction that the nucleus exerts on an electron can be altered by the pressence of another electron only if this second electron is between it and the nucleus; not by an electron in the same shell. It follows that, if one electron could be removed, the second could be removed just as easily.
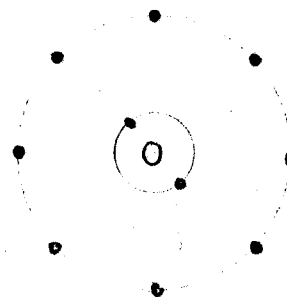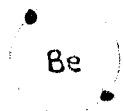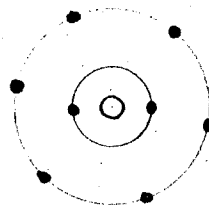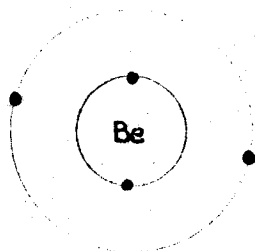
Oxygen can accommodate two more electrons in its outer shell. The addition of these two electrons will not increase the total number to the point where mutual repulsion between the electrons overcomes nuclear attraction. In the example being considered (figure 2.2b) oxygen captures these two electrons from berylium.

The tendency for oxygen to become a negative ion is not as strong as that for florine because the nuclear charge of oxygen is one unit less. The reason that it will take on two electrons is because it can accommodate them in the outer shell, not becuase its holding power is any greater than that of florine.

Covalent Bonding. It follows from the preceeding discussion that an exchange of electrons will take place between atoms with relatively few electrons in the outer shell (which form positive ions) and atoms with an almost full outer shell (which form negative ions). When the number of electrons in the outer shell of the reacting substances are nearly equal, the chemical reaction proceeds somewhat differently. For example, both florine and chlorine have a strong tendency to gain another electron because they both have seven in their outer shells. When the compound chlorine floride is formed, electrons are not completely transfered because neither atom has a strong enough affinity for an electron to remove it from the other atom. Or, conversely, the outer electrons are not so loosely held that they can be removed by either atom. What does happen is that the outer shell electrons are shared. The two atoms are joined together, and the outer shell electrons assume some complex orbit about both atoms instead of around the individual atoms. This gives rise to a force which binds the two together forming a molecule. This binding force is refered to as a covalent bond. The chlorine floride molecule is shown in figure 2.3a.

a. Lithium and Florine React to Form Lithium Floride.

b. Berylium and Oxygen React to Form Berylium Oxide.

Figure 2.2. Illustration of Chemical Reactions in which Complete Electron Transfer Takes Place.
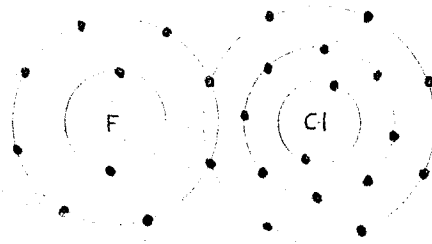
Other examples of covalent bonding are given in figures 2.3b and 2.3c. The first illustrates the result of a reaction between hydrogen and oxygen to form water. The second shows the product of a reaction between carbon and chlorine. In both cases, neither of the reacting substances will gain or loose electrons. The outer shell electrons are shared, not transfered. After the reaction, all the outer shell electrons apparently orbit around the entire molecule in a distorted path, rather than about the individual atoms.

Stable Electron Configurations. The inert gasses will serve as a foundation for the following discussion. It can be seen from figure 2.1 that the outer shell of the inert gasses listed (helium, neon, and argon) are apparently complete since the following element on the periodic chart starts a new shell. These gasses are chemically inactive in that they will not react with any known substance. Therefore, it appears that a completed electron structure is very stable.
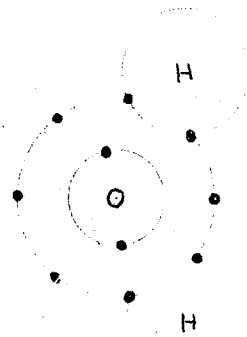
There is one thing in common in all the reactions mentioned thus far. The outer shell electrons were rearranged to produce a completed outer shell in all the reacting substances similar to that of the inert gasses. This is true whether there was a complete transfer of electrons to form ions or a sharing of electrons to form a molecule. For example, the lithium atom in figure 2.2a looses an electron thereby assuming the stable electron configuration of helium. The florine atom, which gained the electron, assumes the stable configuration of neon. The same is true for the berylium and oxygen atoms in figure 2.2b. Electron sharing produces similar results as can be seen from figure 2.3. In the first example (chlorine floride), sharing of the outer shell electrons produces a stable electron structure in both the chlorine and florine (that of argon and neon, respectively). The same is true in the other examples.

A chemical reaction will normally produce a stable electron structure in the reacting substances. If not, the reaction products are themselves unstable and will usually decompose into a compound which does have a stable structure.

Other Chemical Properties. More information can be gathered from a further study of the atom. The chemistry of an element is not solely determined by the number of electrons in the outer shell, although this does appear to be the most important factor. The atomic number of the element is also important. For example, lithium, sodium, and potassium have one electron in their outer shell and all three tend to loose it readily. However, potassium looses it most easily while sodium is next and lithium last. This can be explained. The lone outer electron of potassium is better shielded by three completed electron shells than is that of either sodium or lithium, which have fewer completed shells. The same trend is evidenced with chlorine and florine. Both these atoms tend to gain an extra electron, but florine has the strongest tendency because

a. Chlorine Floride Molecule.

b. Water Molecule.

c. Carbon Tetrachloride Molecule.

Figure 2.3. Three Examples of Atoms Held Together by Covalent Bonding.

its nucleus is shielded by one less electron shell than is chlorine. Generally, in different elements with the same number of outer shell electrons, those with the higher atomic number will loose electrons more readily or gain them less easily. This fact becomes important later in explaining the difference between different semiconductor materials, namely germanium and silicon.

BINDING FORCES IN SOLIDS

When sodium reacts with chlorine, two ions will be formed. After the reaction has completed,these ions will join together to form solid sodium chloride. Their net positive and negative charges will set up an electrostatic force of attraction which holds the atoms together in the solid form. This binding force is known as an ionic bond.

Solids can be formed in several ways, ionic bonding being only one example. Water molecules (figure 2.3b) are held together in ice by forces of a different origin. Each molecule has a net charge of zero, but the molecule behaves like an electric dipole: Negative on one end and positive on the other. The outer electrons shared by both the hydrogen and oxygen are displaced somewhat toward the oxygen because of its greater affinity for electrons. This end of the molecule becomes negative with respect to the end containing the two hydrogen atoms. When water freezes to form ice, the molecules become lined up and are held in place by the polar forces.

When two neutral atoms are brought into close proximity, the electron cloud of each will cause a net repulsion. However, if they are brought even closer, the positive charges of the nuclei will act through the electron cloud and produce a net attraction: The nucleus of one atom will attract the electron cloud of the other. This is how some elemental solids are held together. For example, in one form of carbon, lampblack, the individual atoms are held together by this type of attractive force.

The kind of binding force that will be of primary interest from this point on is the covalent bond. Solids can be held together by one continuous covalent bond. This is the force that holds together practically all elemental metals and infermetalics. Carbon will serve to illustrate the characteristics of the covalent bond: As mentioned above, lampblack is held together by rather weak attractive forces. Another form of carbon, diamond, is held together by a continuous covalent bond. A third form, graphite, is held together by a combination of these forces. Graphite is made up of molecular layers of carbon atoms. In each layer the atoms are held together by covalent bonds, but between the layers the forces are the same as for lampblack. This accounts for the fact that graphite can be easily split along certain planes. An interesting point is that both lampblack and graphite are conductors while diamond is an excellent insulator.

CRYSTALS

The atoms of crystals are arranged in a definite, orderly, and continuous pattern. On the other hand the atoms of some solids known as glasses, are arranged in a haphazard fashion. The difference between these two substances is evident when they are melted and then cooled. A crystal will go from the liquid to the solid form at a definite temperature known as the freezing point, but a glass will become thicker and thicker before it finally hardens. This does not occur at any definite temperature. When a crystal freezes, it liberates a certain amount of heat (heat of fusion). If the crystal is then remelted, the heat of fusion must be supplied to the crystal before it will melt. This indicates that the binding forces in crystals are generally stronger than those of glasses since this energy in the form of heat must be supplied to break the bonds and melt the crystal.

Sodium chloride is an example of a crystaline solid. Each sodium ion is surrounded by six chloride ions, and each chloride ion is surrounded by six sodium ions. This pattern persists throughout the crystal, being broken only at the surface.

Water will form ice crystals as it freezes. The polar water molecules align themselves in an orderly pattern and produce a continuous crystal structure.

Most important in the study of semiconductors is the completely covalent crystal. In this case the entire crystal is held together by a single continuous covalent bond. Carbon, silicon, and germanium can form such crystals.

When carbon atoms join together to form a diamond crystal, the four outer shell (valence) electrons engage in a covalent bond. This is not unexpected considering that all these atoms have an equal tendency to gain or loose electrons. Figure 2.4 illustrates the bonding of a diamond crystal. Each carbon atom shares electrons with four of its neighbors in such a way that the electron structure of each atom becomes completed. A pictorial view of the space arrangement of the atoms in a carbon crystal is given in figures 2.5 and 2.6. Figure 2.5 shows the orientation of atoms about a central atom. This arrangement is repeated in the complete crystal as shown in figure 2.6. The covalent bonding and crystal structure of silicon and germanium is similar to this since they also have four electrons in their outer shell. The strength of the covalent bonds becomes progressively weaker going from carbon to silicon to germanium. This is probably due to the presence of an additional inner electron shell on each of these atoms.
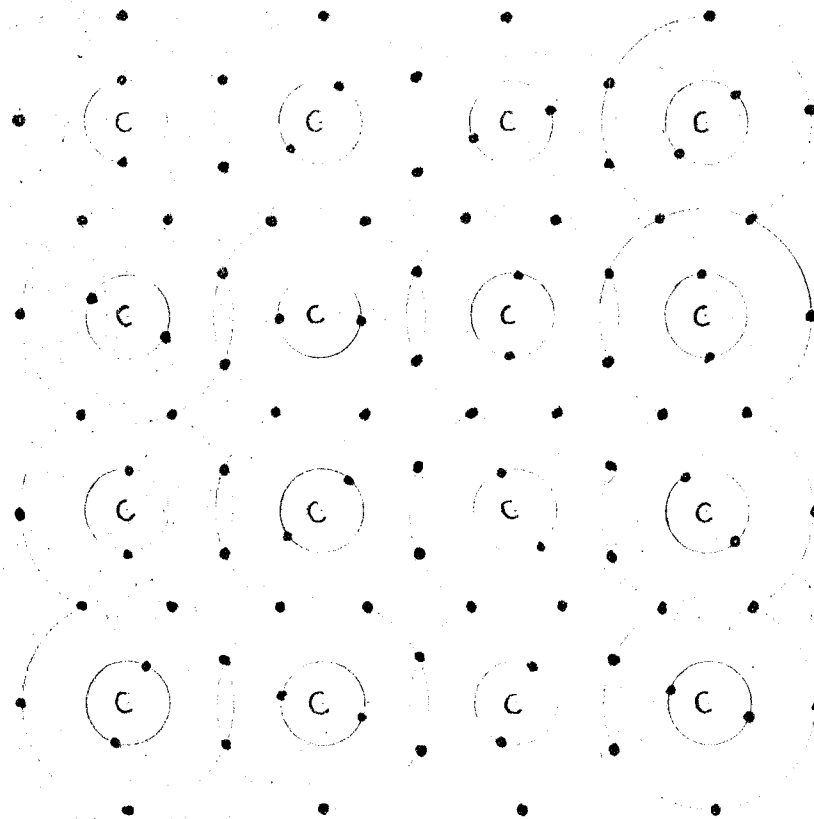
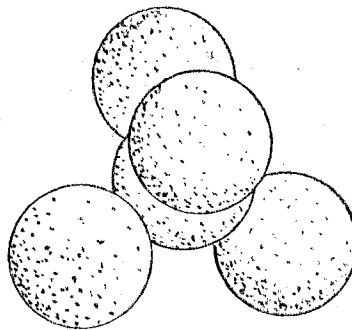Figure 2.4. Schematic Representation of Covalent Bonding in a Diamond Crystal.

Figure 2.5. Illustration of Atomic Arrangement Around a Single Atom in a Carbon, Silicon, or Germanium Crystal.

When molten silicon or germanium (individual atoms) freeze to form a crystal, energy in the form of heat is released (heat of fusion). This energy must have gone into the formation of covalent bonds since the configuration of the outer electron shell is the only change brought about by this process. It follows that energy must be supplied to break the covalent bonds whether it be thermal energy in melting the crystal, mechanical energy in breaking the crystal, or electrical energy in ionizing electrons from the covalent bonds.

It appears that the electron structure of these crystals is quite stable. Electrons cannot be added to the completed valence structure, nor can they be removed without supplying energy to break the bonds.

Internal Electric Fields. The electric field close to a neutral atom is not zero. However, when many of these atoms are brought close together, the individual fields will neutralize, creating regions of negligible electric field. In the crystals being considered, the space between atoms is electrically neutral, as is the region occupied by the outer shell or valence electrons. This shows why the valence electrons are not attracted to any particular nucleus and are free to roam about the entire crystal; the only force holding them in the outer shell structure is the covalent bonds. If an electron is excited or broken away from the covalent bonds it will move about in the free space between atoms until it finds a vacancy in the covalent bonds. It will then give up the energy it gained in breaking loose and go back into the valence structure.

External Electric Fields. At low temperatures, the covalent bonds of carbon, silicon, and germanium crystals are complete. When an electric field is applied across these crystals, the valence electrons tend to move in the positive direction of the field. However, before the displacement becomes appreciable, they will be restrained by the covalent bonds. There is no continuous motion of charged particles and no current through the crystal.

Free Electrons. The covalent bonds are not so strong that they cannot be broken by the application of sufficiently high voltages. When very high voltages are applied across the crystal, the electric field tending to move the electrons becomes stronger than the restraining forces of the covalent bonds. When this happens, electrons are broken loose and introduced into the space between the atoms. Here, the only force acting on them is the externally applied electric field, so they move through the crystal under the influence of this field. This motion will not be in a straight line. The electrons will collide with the atoms in moving through the crystal. In these collisions, the electrons do not usually make physical contact with any part of the atoms; but they are deflected by electrostatic forces when they penetrate the outer electron shell. In the process, they give up some of their energy to the atom. This loss of energy accounts for the electrical resistance of the material. Normally, when the electrons

collide with the atoms, they are not retained in the covalent bonds unless there happens to be a vacancy at that point in the crystal. Furthermore, the kinetic energy of the electron must be low enough so that it cannot break loose after it is captured. The motion of a free electron is illustrated in figure 2.6.
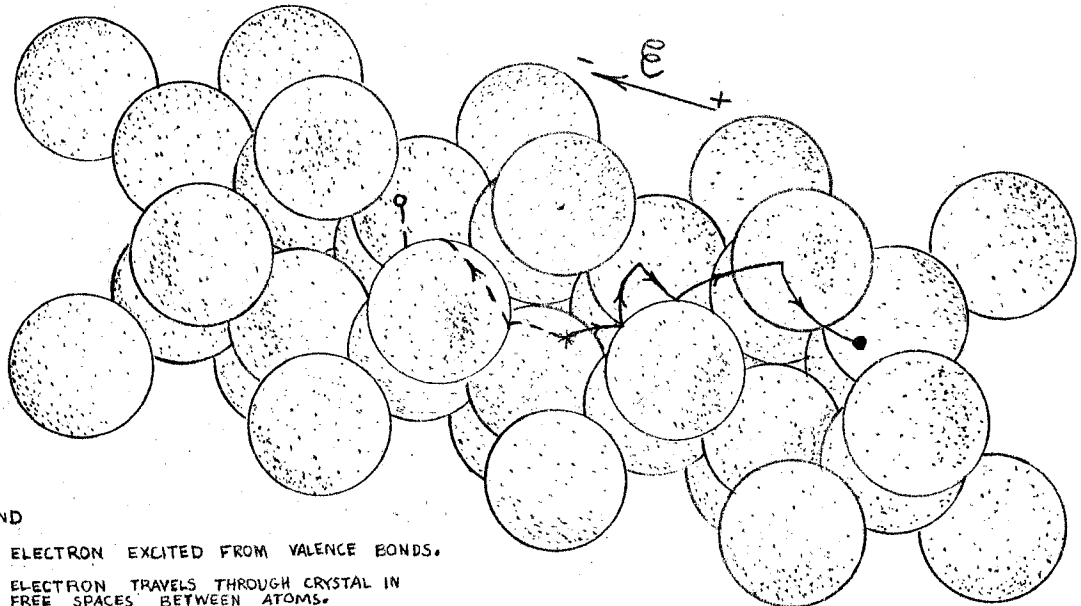
Holes. The movement of free electrons through the crystal accounts for only about half the total current observed. What was introduced as a hole in chapter 1 supplies the remainder.

When the covalent bonds are complete, the valence electrons are free to wander about the crystal: That is, they are not bound to a particular atom so any individual electron can drift from atom to atom as long as it is immediately replaced by another. When a moderate electric field is applied across the crystal, the valence electrons try to move under the influence of the field; but they are restrained by the covalent bonds. Any net motion would remove electrons from some atoms and give others too many, which will not happen because the outer shells of all the atoms are already completed.

If an electron is excited from the covalent bonds, this situation is altered. The removal of an electron from the bonds creates a vacancy, and the valence electrons acted upon in the proper direction by the external field will move in and fill this vacancy. Hence, the gap in the valence structure will move through the crystal in much the same way as the free electrons. It should be remembered, though, that this vacancy is not something tangible. It is just the condition of the covalent bonds at a particular point in the crystal. Conduction is actually caused by the net motion of bound electrons in the outer electron shells.

A good analogy of this action is the motion of a bubble in a glass of water. A bubble released at the bottom of the glass will appear to rise to the surface. However, an exact analysis will show that the water is actually moving downward under the influence of gravity. The bubble is nothing but a void that is filled by water in response to the force of gravity. Similarly, in the crystal, the vacancy seems to move through the continuous electron structure, but the valence electrons are actually moving under the influence of the applied field.

Since this vacancy unbalances the electronic charge distribution in the crystal, it is accompanied by a small positive charge. Therefore, considering only the electrostatic effects on the interior of the crystal, the hole appears to be a small positive charge. When an external field is applied, this charge seems to move toward the more negative portion of the field. Although it is an unbalanced condition that is being displaced, the net effect is the same as if a free positive charge were moving through the crystal.

2-12

LEGEND

* ELECTRON EXCITED FROM VALENCE BONDS.

→• ELECTRON TRAVELS THROUGH CRYSTAL IN
FREE SPACES BETWEEN ATOMS.

→&omp;O VACANCY TRAVELS IN OUTER SHELL ELECTRON
STRUCTURE OF ATOMS.

Figure 2.6. Paths of Free Electrons and Vacancies in the Valence Bonds
Under the Influence of an Applied Electric Field.

Conduction by holes is illustrated in figure 2.6. The vacancy travels in the outer electron shells, but the electrical field from the net positive charge associated with this vacancy permeates the free space between the atoms. Any electric or magnetic fields that exist in the free space will react with this field so the net effect is again that of a free positive charge.

It can be seen that there are two distinct types of current carriers in the crystals discussed thus far: Free electrons and bound valence electrons. However, the valence electrons can only contribute to conduction if there is a vacancy in the covalent bonds. This condition was shown to be equivalent to a free positive charge within the crystal.

THERMAL AGITATION

The molecules of matter are in a continual state of motion. The magnitude of this motion is directly dependent on temperature. For example, if a gas is sealed inside a closed container and the temperature increased, the pressure on the walls of the container will increase. As the gas is heated, the thermal energy abosrbed will increase the kinetic energy of the gas molecules. These molecules will then strike the walls of the container with greater froce, producing the increased pressure.

Other physical evidence of thermal motion is not difficult to find. When a solid is heated above its melting point the individual molecules gain enough thermal energy to break loose from one another, and a liquid is formed. If the temperature is increased further, the molecules will gain enough energy to break away from the liquid surface and move out into the surrounding space to become a vapor or gas. If the temperature is increased still further, the molecules will shake themselves apart into individual atoms. Finally, at very high temperatures, the electrons of these atoms will absorb enough thermal energy to break away from their orbits, producing a gaseous mixture of ions.

From the above example, it appears that thermal motion manifests itself as an oscillation of the individual molecules against the forces binding them together. Furthermore, it appears that all the components of the solid take part in this oscillation: Not only do the molecules vibrate; but the atoms also vibrate, restrained by the forces binding them into molecules; and the electrons vibrate against the attraction of the nuclei.

It follows that in the crystals being considered (carbon, silicon, and germanium) the atoms are not in a fixed position at normal temperatures, but are oscillating about a mean position because of their thermal energy. Moreover, the valence electrons are oscillating against the restraining forces of the covalent bonds. In both these cases, the amplitude of oscillation is some function of temperature, increasing with increasing temperature.

Energy Distribution. When all the heat is removed from a substance,
thermal motion ceases. The temperature corresponding to this condition
is called absolute zero (-273°C). At this temperature, the atoms of a
semiconductor crystal will be fixed in a neat, orderly array as shown in
figure 2.6. At any temperature above absolute zero, the atoms will
oscillate about their original positions, the amplitude increasing with
increasing temperature. The average thermal energy of all the atoms
is well defined since only a certain amount of thermal energy was put
into the crystal in raising its temperature. However, because it is
possible for one atom to collide with another and give up part of its
energy (whether the collision is physical or an electric field
interaction), the energy of the individual atoms can vary. These collisions
will be completely random so it is possible for some atoms to loose all
their thermal energy and for others to gain energy from several collisions.
The energies of the individual atoms can therefore range from zero to
several times the average thermal energy.

Observation has shown that most crystals melt at a definite
temperature which indicates that almost all the atoms gain enough
thermal energy to break loose from the covalent bonds at approximately
the same temperature. This means that the energy distribution about the
average value will be relatively narrow. Very few atoms will have
energies very much higher than the average value and very few will
have energies much lower than average. The narrow distribution
indicates that the frequency of collision between atoms is not too
great.

The valence electrons will also have a certain amount of thermal
energy in addition to their kinetic energy of motion in the outer
electron shells. Again this energy is not the same for all electrons, but
is distriubted about some average value as a result of interactions
between electrons and between electrons and atoms. Hence, at any
temperature above absolute zero, an individual electron may have any
amount of thermal energy from zero to many times the average value.

Thermal Ionization. If an electron gains sufficient thermal energy,
it is possible for it to break loose from the covalent bonds and be
introduced into the free spaces between atoms. This process involving
the thermal generation of hole-electron pairs is refered to as thermal
ionization. It is similar, in effect, to the production of hole-electron
pairs with strong electric fields, except that the ionization energy is
supplied by the thermal motion of the electrons rather than an electric
field.

At low temperatures there will be very few electrons with enough thermal energy to break the covalent bonds. As temperature increases, this number will increase quite rapidly. However, even at high temperatures, only a very small percentage of the outer shell electrons will become ionized.

Before going further, it would be enlightening to consider the magnitude of these thermal effects. For example, in a germanium crystal at -125°C, there are about 8×10^{6} hole-electron pairs per cubic centimeter. This is quite a large number, but there is only about one thermal ionization for every 2×10^{14} germanium atoms. At this temperature, germanium is an excellent insulator. Near room temperature (30°C) there are about 2×10^{13} hole-electron pairs per cubic centimeter or one ionization in 5×10^{10} atoms. Even at the highest operating temperature of practical germanium devices (100°C), there are about 10^{15} ionizations per cubic centimeter or one in 10^{9} atoms. At these temperatures, germanium is a poor isulator; but it is still far from being a conductor. In a conductor each atom donates several free electrons to the metalic crystal giving about 10^{28} free electrons per cubic centimeter.

After an electron is ionized from the covalent bonds, it does not remain stationary in the interior of the crystal; but it will wander through the crystal with a random, erratic motion, encountering frequent collisions with the atoms. This motion arises from the thermal energy of the electron. Similarly, the holes created by this process also move about the crystal with a radom motion because of the excess thermal energy of the valence electrons. However, in neither case does this motion constitute a current. On an average, there are as many current carriers moving in one direction as there are in another, so there is no net transfer of charge.

If an electric field is applied through the crystal, the random thermal motion of the holes and electrons will be modulated by a net motion in the direction of the field. The magnitude of the current for a given field strength (conductivity) will obviously depend on the number of carriers available and on their average forward velocity in the direction of the field. For a given field strength, the forward velocity of the current carriers will depend on the number of collisions suffered by the carriers in moving through the crystal. At low temperatures, the collisions will be relatively infrequent, being caused only by the forward motion of the carriers. At higher temperatures, the thermal motion of the atoms and electrons will increase the frequency of collision and, therefore, reduce the forward velocity.

This affords another distinction between pure semiconductors and metalic conductors: In a conductor, there are generally several outer shell electrons per atom that are not required to complete the covalent bonds. These electrons are free to move through the crystal under the influence of an externally applied electric field and can therefore support a current. The number of current carriers will remain essentially constant with temperature since there is already a huge number available and any small addition from thermal ionizations would be insignificant. Hence, as temperature is increased, the only effect on the conducting properties of the crystal is the restricted motion of the free electrons arising from the increased thermal motion. It follows that the conductivity will decrease with increasing temperature. For most metals, the conductivity is found to decrease at the rate of about 0.3 per cent per degree increase in temperature.

In a semiconductor, the number of current carriers does not remain constant, but increases enormously with temperature. As temperature is increased, the increased concentration of carriers affects the conductivity much more than does the restricted motion. Hence, a semiconductor has a negative temperature coeficient: That is, the conductivity increases with increasing temperature. Furthermore, the magnitude of this change is considerably greater than the change in metals. For germanium near room temperature, there is about a 5 per cent increase in conductivity per degree increase in temperature.

Thermistors. In diodes and transistors, the temperature sensitivity of semiconductor materials is moderated by the addition of impurities as will be shown in the next section. There are, however, a class of semiconductor devices known as thermistors (negative temperature coeficient resistors) that make use of this large change in conductivity with temperature. Thermistors have found application as temperature sensors and as compensating elements in transistor circuits.

EFFECTS OF IMPURITIES ON ELECTRICAL CONDUCTIVITY

It was shown in chapter 1 that diodes and transistors were constructed of P-type materials, having holes for current carriers, and N-type materials, having electrons for current carriers. In the pure semiconductor crystals considered thus far the number of holes and electrons were equal; however, these pure crystals can be given P or N-type characteristics by the addition of suitable impurities.

N-Type Crystals. If a small amount of phosphorous, arsenic, or antimony is added to a germanium crystal during the growth process, its conductivity at room temperature will be much greater than that of a pure crystal. Furthermore, tests carried out on this crystal will show that there are far more free electron current carriers than there are holes. This can be explained by considering the effect of these impurities on the electronic structure of the crystal.

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The outer electron shells of phosphorous, arsenic, and antimony atoms contain five electrons. If these atoms are introduced into the crystal in small quantities, they will replace germanium atoms in the crystal structure; and their outer shell electrons will take part in the covalent bonding in much the same way as the germanium atoms, except that there will be one electron left over which is not required to complete the bonds. This is illustrated in figure 2.7.

At very low temperatures this fifth electron is held to the impurity atom by the extra positive charge of its nucleus. However, the electrostatic forces holding this electron are much weaker than those of the covalent bonds. At relatively low temperatures, the thermal energy of this electron will overcome the electrostatic forces binding it to its parent atom so it will break loose and wander through the crystal with a random thermal motion. Thus, free electrons are introduced into the crystal without creating holes; and a N-type crystal is produced.

P-Type Crystals. When impurities such as aluminum, gallium, or indium are added to a germanium crystal, the conductivity will also increase greatly. However, the current carriers will be holes; the number of free electrons will be negligible. This behavior is not difficult to reconcile. These impurities (aluminum, gallium, and indium) have three outer shell electrons. When they are added to a germanium crystal in small quantities, they will take the place of a germanium atom in the crystal structure; but, in the formamation of the covalent bonds, there will be a gap left near the impurity atom because of the absence of a forth outer shell electron (figure 2.8). At very low temperatures, this vacancy in the covalent bonds will be fixed to the impurity atom because of its lesser net charge. However, even at low temperatures, the thermal energy of the valence electrons will become great enough to overcome this differential in net atomic charge. Other valence electrons will then be able to move in to fill this vacancy, and it will range through the crystal with a random thermal motion. Hence, free holes are produced in the outer shell electron structure, giving a higher concentration of hole carriers than electron carriers.

It can be seen that the addition of suitable impurities to a semiconductor crystal will produce either P or N type material. The process of adding controled amounts of impurities is refered to as doping. The group V impurities (phosphorous, arsenic, and antimony) are called donars because they donate a free electron to the electronic structure of the crystal. The majority carriers in this N-type crystal will be electrons. The group III impurities (boron, aluminum, gallium, and indium) are called acceptors because they can accept an electron to complete their covalent bonds. These impurities will, therefore, produce vacancies in the outer shell electron structure, or hole current carriers. In such a crystal (P-type) the holes are called majority carriers.
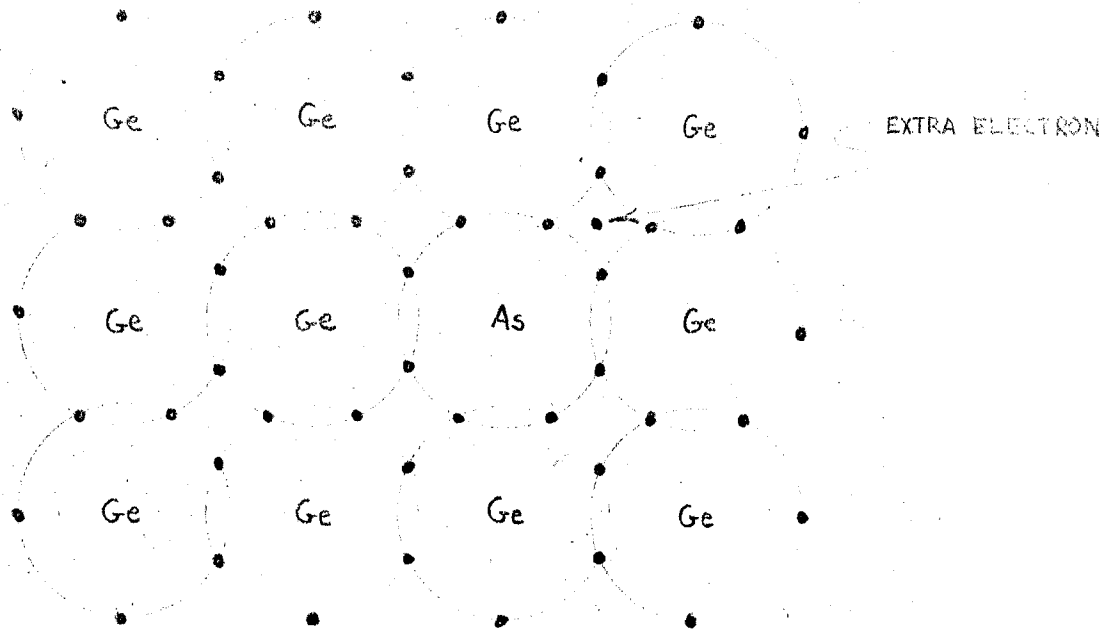
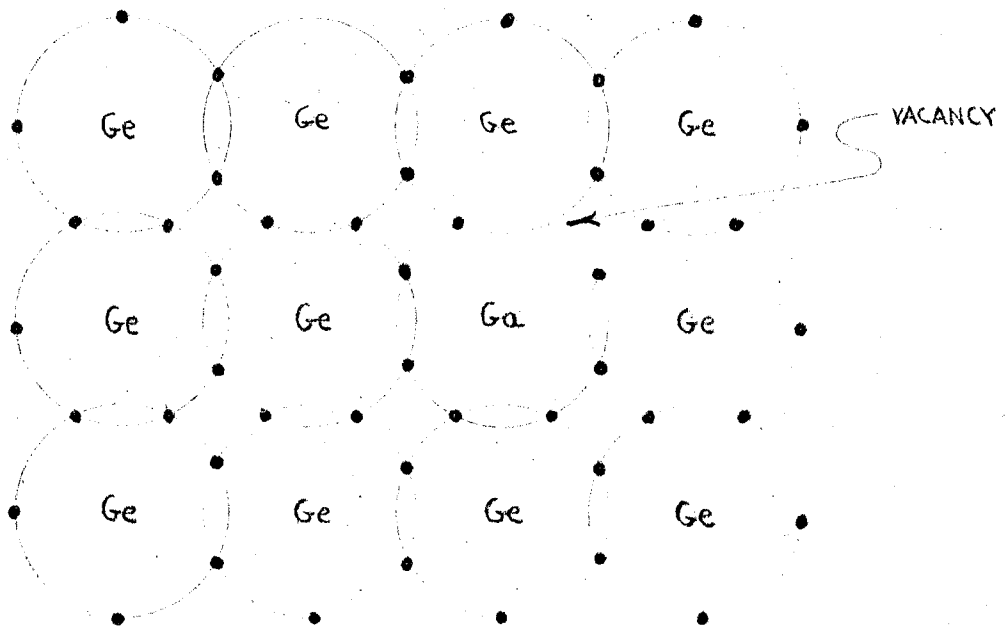Figure 2.7. Covalent Bonding of an Arsenic Impurity in a Germanium Crystal.

Figure 2.8. Covalent Bonding of a Gallium Impurity in a Germanium Crystal.

Only a small amount of impurities can be added if a continuous crystal structure is to be maintained. The usual concentration is around 10^{16} impurity atoms per cubic centimeter, or about one in 10^8 germanium atoms. If the impurity concentration is made much greater than one part per million, the desirable properties of the crystal will be destroyed by the local electric fields associated with the impurity atoms.

Effect of Temperature on Doped Crystals. It has already been stated that the conductivity of a pure semiconductor crystal increases rapidly with temperature. This characteristic is modified by the presence of impurities as is shown in figure 2.9 where the variation of conductivity with temperature is plotted for both doped and undoped crystals.

At temperatures near absolute zero very few of the current carriers provided by the impurity atoms will be available for conduction. The thermal energy of these carriers is not sufficient to overcome the unbalanced electric field near the impurity atoms (the net charge of a donor impurity is one unit greater than the atoms of the host crystal and that of an acceptor is one unit less). As temperature is increased, the carriers will gain enough thermal energy to break away from the impurity atoms. This process is called impurity ionization and is responsible for the sharp increase in conductivity shown in figure 2.9. A temperature will soon be reached ($-225°C$ to $-175°C$) where practically all the impurities become ionized; further increases in temperature will not significantly increase the number of current carriers. In this region (extrinsic region) the conductivity will drop somewhat because increased thermal motion improves the probability of collision between the current carriers and the immobile atoms, thus reducing their average velocity for a particular applied field.

At high temperatures (about $100°C$ for germanium, or $200°C$ for silicon), the number of thermal ionizations from the covalent bonds becomes appreciable. This will increase the number of current carriers so the conductivity will again increase as shown in figure 2.9. In this region, thermally generated hole-electron pairs, as well as the majority carriers provided by the impurities, will contribute to any current through the crystal. Since the operation of most semiconductor devices depends on the existence of a majority carrier, the semiconductor is rendered useless in this region. This phenomenon is responsible for the sometimes severe temperature limitations imposed on diodes and transistors.

Figure 2.9 shows that the extrinsic region can be extended over a wider temperature range by increasing the impurity concentration. This improvement is greater than might be expected: At a given temperature the minority carrier concentration is lower in a heavily doped crystal. The presence of a larger number of majority carriers increases the probability of recombination between majority and minority carriers (holes and electrons or vice versa) and therefore suppresses the minority carrier concentration. This fact is utilized to improve high temperature performance of semiconductor devices, but it cannot be considered a cure-all since an increased impurity concentration may deteriorate other desirable characteristics.
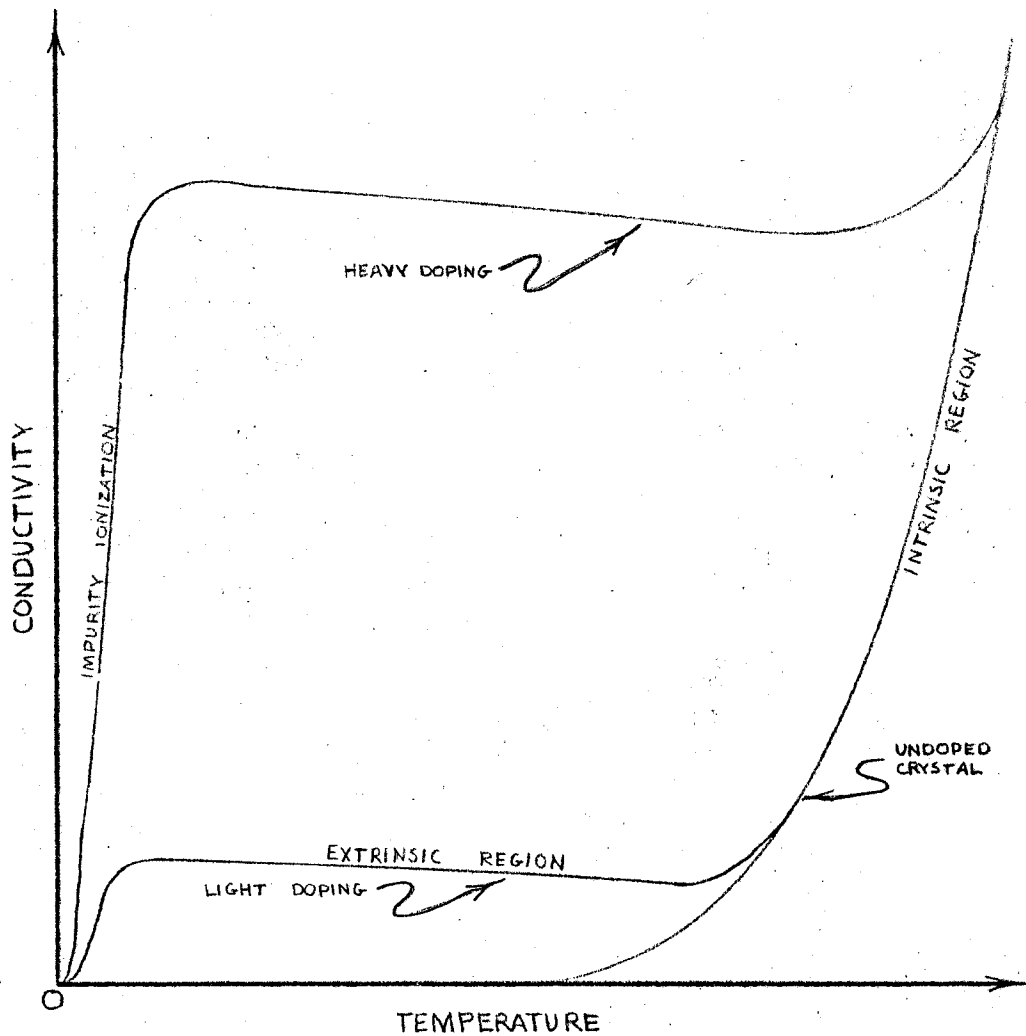
Figure 2.9. Variation of Conductivity with Temperature for Semiconductor Crystals Having Different Impurity Concentrations.

MECHANISMS OF CONDUCTION IN SEMICONDUCTORS

If an electric field is applied across a semiconductor crystal
containing mobile current carriers, a net motion in the direction of the
field will be superimposed on the random thermal motion of the carriers.
This is illustrated in figure 2.10. The average velocity in the
direction of the field will depend on the electric field intensity and
the ease with which the carriers can move through the material. This
latter quantity is defined as the mobility of the current carriers.
Mobility will depend on the number of collisions suffered by the carriers
in moving through the crystal and will, therefore, be a function of
temperature. The average forward velocity is called the drift velocity,
and the process of conduction by mobile carriers in an electric field is
refered to as drift in a potential gradient where the potential gradient
is the change in electric potential with distance through the crystal, or
the electric field intensity. Drift is only one possible mechanism of
conduction; it is also possible to establish a current in the absence
of an electric field.

Thermal Diffusion. If a volume contains a large number of particles
moving with a random thermal motion, there will be a force present to
equalize the distribution of particles throughout the volume. Considering
only a small element of the total volume, the number of particles moving
out of the element will be porportional to the number of particles
contained by the element since the motion is entirely random. Similarly,
the number of particles moving into the element will be porportional to
the particle density in the surrounding volume. It follows that if the
density of one of these regions differs from the density of the other,
there will be a net motion of particles from the region of high density
to that of lower density. This process will continue until the densities
become equalized; then there will be as many particles moving in one
direction as there is in the opposite direction and no net motion.

The process involving the net transfer of particles from regions
of high density to regions of low density, driven by thermal forces, is
called diffusion. The rate of diffusion will be porportional to the
density gradient which is the variation of density with distance through
the volume. The diffusion rate is also dependent on the magnitude of
the thermal motion and is, therefore, dependent on temperature.

The diffusion process is illustrated in figure 2.11. Specific
examples are not difficult to find: If a gas is released in an
evacuated container, it will diffuse through the container until a
uniform distribution is reached. It should be evident that this is
a thermal diffusion process since the gas will condense into a liquid
if the temperature is lowered enough. The laws of diffusion also hold
if there is a nonuniform distribution of one substance within another.
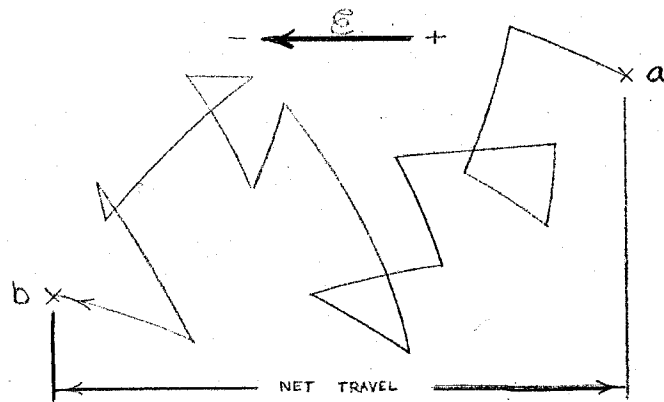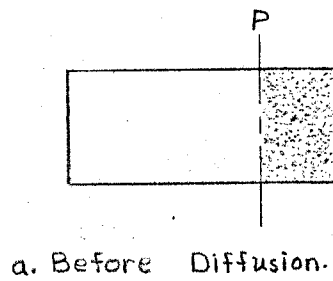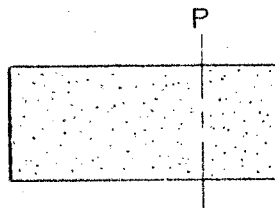
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Figure 2.10. Modulation of the Random Thermal Motion of a Hole by an Electric Field.

a. Before Diffusion.

b. After Diffusion.

Figure 2.11. Thermal Diffusion of Uncharged Particles to Equalize Distribution.

For example, if ammonia gas is released into the atmosphere it will
diffuse to equalize its distribution. The same is true for a drop of
ink in a glass of water, or even for two solids in contact. However,
in these examples, the diffusion rate will not only depend on the density
gradient and the temperature, but it will also depend on the ease with
which one substance can move through the other.

     <u>Diffusion of Charged Particles</u>. The discussion thus far refered to
the thermal diffusion of uncharged particles. Diffusion forces will also
act on charged particles. However, the electric fields produced by the
displacement of the particles must be considered. If a doped
semiconductor crystal is brought into contact with an undoped crystal,
current carriers will diffuse from the doped to the undoped crystal
because of the density variation; but the current carriers moving into
the undoped crystal will set up an electric field which will oppose
further diffusion. This is only one example of a combination of thermal
and electrical forces acting on charged particles; others will become
apparent in later chapters.

     When holes are injected into a N-type crystal one end of which is
connected to a sink (ground) as shown in figure 2.12a, an electric field
will be set up by the excess positive charge. (Note: How this injection
takes place is of little importance here, but an example has already
been given in chapter 1 where holes were injected into the N-type base
of a transistor by forward biasing the emitter base junction.) Both
the injected holes and the free electrons will be acted upon by this
field and will move through the crystal. The end result is illustrated
in figure 2.11c. Before the holes can move very far into the crystal,
the free electrons will move in and neutralize the electric field; the
extra electrons needed to accomplish this being drawn in from the sink.
This phenomenon is known as <u>space charge neutralization</u> since it
neutralizes the excess charge produced by carrier injection (analagous
to the space charge around the cathode of a vacuum tube). The suppression
of this charge permits the injection of large currents at relatively low
voltages and is partly responsible for the high efficiency of semiconductor
devices.

     <u>Diffusion Current</u>. After space charge neutralization takes place,
there will be no net electrostatic force acting on the current carriers.
Within the crystal, the holes are neutralized locally by the presence of
excess electrons; however, these electrons will not recombine immediately
with the holes (fall into the valence vacancies) since their energy is
too high. In the absence of an electric field, the holes will be acted
upon solely by thermal diffusion forces and will diffuse through the
crystal toward the sink, since the hole density is lower in this region.
If the hole injection is continued, a current will be established through
the crystal without the aid of an electric field; this is called a
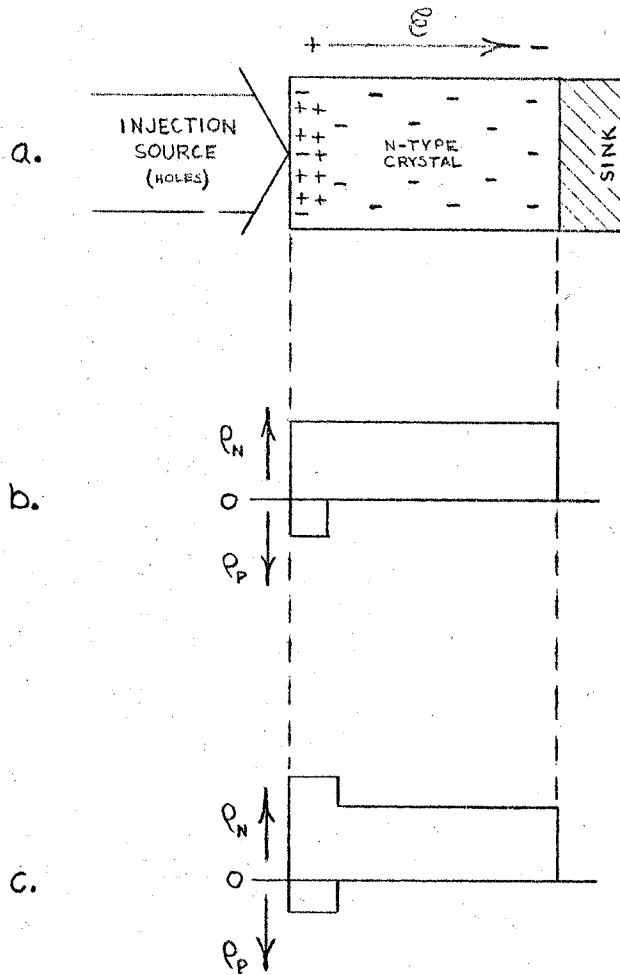<u>diffusion current</u>.

Figure 2.12. Electric Field Produced by Injection of Minority Carriers (a). Density of Holes (ρ_P) and Electrons (ρ_N) with Distance through Crystal before Space Charge Neutralization (b). Neutralization of Electric Field by Displacement of Majority Carriers (c).

If holes are injected at a constant rate, they must also diffuse through the crystal at a constant rate to prevent an accumulation of charge. When the number of recombinations is negligible, this requires linear variation of hole density with distance through the crystal so that the diffusion rate will be constant. This condition is shown in figure 2.13a. The entire current is carried by the diffusion of holes: The electrons remain fixed to neutralize the excess charge.

Recombination. If the diffusion path is made sufficiently long, the number of recombinations will become significant, particularly if the crystal contains many defects at which the free electrons can loose their excess energy and fall into the valence vacancies. The average time that a minority carrier can exist in a crystal containing a majority carrier is defined as the minority carrier lifetime and is a measure of crystaline perfection. For crystals of good quality, the minority carrier lifetime ranges from 10 to 1000 ys.

Under conditions of appreciable recombination, the density distribution shown in figure 2.15b can be expected. Here, current is carried both by holes diffusing into the crystal from the injection source and by electrons moving in and recombining with the holes. The sum of the hole and electron currents must be equal to the total current at any distance down the crystal: Current is carried almost entirely by holes near the injection source and almost entirely by electrons near the sink. The average distance that a minority carrier can travel into the crystal before recombination occurs is defined as the diffusion length. This quantity is of particular importance in a transistor; the base width must be much less than the diffusion length to minimize the number of recombinations in the base region.

Conclusions. It has been shown that there are two mechanisms of conduction in a semiconductor: Drift in a potential gradient and diffusion in a density gradient. It is possible for both of these mechanisms to act simultaneously, even with one opposing the other. In any event, the drift current will be directly porportional to the potential gradient, the number of current carriers involved, and the carrier mobility; and the diffusion current will be a direct function of the density gradient, the number of carriers setting up this gradient, the absolute temperature, and the carrier mobility. These mechanisms are of equal importance. The operation of semiconductor devices cannot be adequately explained unless both are given due consideration.

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SEMICONDUCTOR MATERIALS

Thus far, the discussion of semiconductor materials has been confined to those elements having four valence electrons which form a completed electron structure as shown in figure 2.4. These are the group IV elements listed in table 2.1. Nonetheless, combinations of elements will sometimes exhibit semiconductor properties; and the semiconductor properties can usually be predicted by analyzing the electron structures of the combining atoms. For example, if a crystal is composed of an equal number of group III and group V elements, it can exhibit semiconductor properties. This happens because the atoms with five valence electrons will donate an electron to the atoms with three valence electrons in the formation of covalent bonds. The electronic structure will then be similar to that of a group IV crystal. Semiconductor properties also arise from combinations of group II and group VI elements. In this case, the atoms with six valence electrons donate two to the atoms with only two valence electrons, again forming the completed electron configuration of group IV crystals. Compounds of group I and group VII will not show semiconductor properties since a complete transfer of electrons takes place forming ionic rather than covalent bonds. This will sometimes happen in the group II-VI and group III-V compounds.

In group IV crystals, it is necessary to add impurities to produce majority carriers; however, in semiconductor compounds, this can be accomplished by increasing the concentration of one element with respect to the other. To illustrate, if there is an excess of the group III element in a group III-V compound, there will be a deficiency of electrons in the covalent bonds so the crystal will be N-type. If there is an excess of the group V element, electrons will be left over after the covalent bonds are formed so the crystal will be P-type.

Other covalent bond structures can give rise to semiconductor characteristics. Selenium and tellurium in group VI exhibit semiconductor properties, as do compounds like lead sulfide and lead telluride. Semiconductors have also been made from combinations of three or more elements. The valence structure of these elements is not similar to that of the group IV crystals, but is quite complex. Little is known about them at the present time which accounts for the fact that they are not too widely used.

Characteistics of Materials. Although there are a large number of semiconductor materials, relatively few of them are presently being used. The major problem with most materials is the difficulty in producing crystals of adequate purity and perfection. This is more or less a problem of techniques and can probably be solved for a particular material if it shows enough potential.
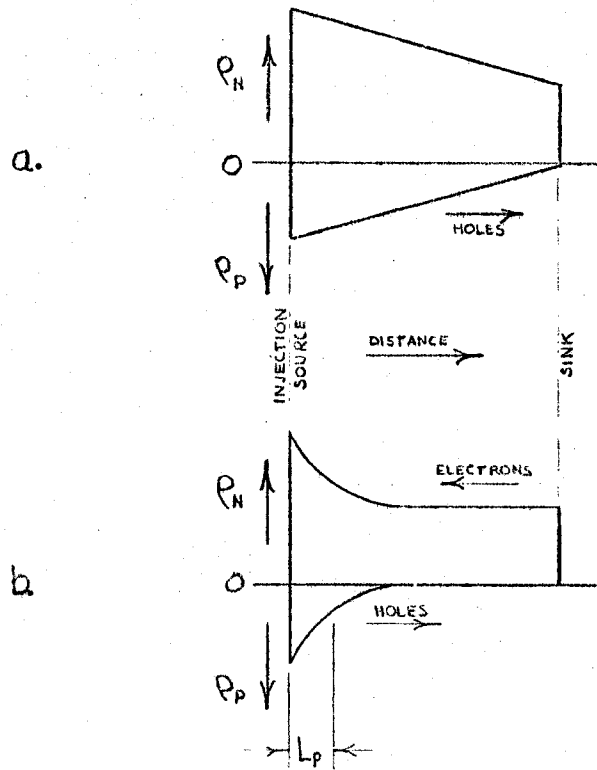
Figure 2.13. Distribution of Current Carriers through a Crystal for a Constant Diffusion Current (a) when there is Negligible Recombination and (b) when there is Appreciable Recombination.

The usefulness of a semiconductor material is ultimately detemined by its physical characteristics. The most important of these are the energy required to ionize electrons from the covalent bonds, which determines the maximum operating temperature, and the mobility of the current carriers. These quantities are given for several materials in table 2.2.

Ionization Energy. The ionization energy is the minimum amount of energy that will free an electron from the covalent bonds. This quantity is zero for a metalic conductor, several electron volts for an insulator, and about one electron volt for a semiconductor. For most applications a high ionization energy is desirable to limit the number of thermally generated hole-electron pairs, since the desirable properties of the semiconductor generally depend on the existence of a majority carrier. If tables 2.1 and 2.2 are compared, a definite trend is evidenced: Semiconductors composed of elements with a low atomic number will have high ionization energies while those composed of elements with high atomic numbers will have low ionization energies. This can be explained by considering the atomic structure. Elements with high atomic numbers will have a greater number of electrons shielding the positive charge of the nucleus. Therefore, the outer shell electrons will be more loosely bound. This is carried over in the formation of covalent bonds.

With elements of higher atomic number, the covalent bonds are sometimes formed in the inner electron shells (secondary velances). This will explain why lead and some forms of tin are metalic conductors, showing no semiconductor properties.

The above discussion is not meant to imply that semiconductors having low ionization energies are useless. In some applications a low ionization energy is required. For example, infared radiation can be detected when it produces ionizations in the covalent bonds of a semiconductor, thus increasing its conductivity. The energy of these radiations is in the order of 0.3 electron volt so a semiconductor that has an ionization energy lower than this value must be used. In these applications, the random thermal ionizations are usually reduced by cooling the crystal to liquid nitrogen temperatures (-196°C).

Mobility. It is desirable that the carrier mobility in a semiconductor be as high as possible since both drift velocity and diffusion rate are dependent on this quantity. Furthermore, if a semiconductor is to be used in a diode, transistor, or any other device where holes and electrons carry current simultaneously, both the hole and the electron mobilities should be high. Table 2.2 shows that there is a wide varience in mobilities for different materials. Some speculation can be made to explain these variations on the basis of atomic structure. Certain trends can be established by examining table 2.2:

Table 2.1. List of Selected Elements from the Periodic Chart.

GROUP				
II	III	IV	V	VI
4 BERYLIUM	5 BORON	6 CARBON	7 NITROGEN	8 OXYGEN
12 MAGNESIUM	13 ALUMINUM	14 SILICON	15 PHOSPHOROUS	16 SULPHUR
30 ZINC	31 GALLIUM	32 GERMANIUM	33 ARSENIC	34 SELENIUM
48 CADMIUM	49 INDIUM	50 TIN	51 ANTIMONY	52 TELLURIUM
80 MERCURY	81 THALLIUM	82 LEAD	83 BISMUTH	84 POLONIUM

Table 2.2. Characteristics of Some Semiconductor Materials.

GROUP	MATERIAL	IONIZATION ENERGY (eV)	MOBILITY (cm^2/volt·sec)	
			HOLES	ELECTRONS
IV	Carbon	6.0	1200	1800
	Silicon Carbide	3.0	10	50
	Silicon	1.1	500	1200
	Germanium	0.7	1900	3800
	Tin	0.08	1000	2000
III, V	Aluminum Antimonide	1.6	300	1200
	Gallium Arsenide	1.4	250	4000
	Indium Phosphide	1.25	650	3400
	Gallium Antimonide	0.8	850	4000
	Indium Arsenide	0.4	200	30,000
	Indium Antimonide	0.18	1250	77,000
II, VI	Zinc Oxide	3.2	180	200
	Cadmium Sulfide	2.4	————	210
	Mercury Selenide	0.16	————	15,000

(1) mobility will generally be higher in crystals containing atoms of greater atomic weight, (2) electron mobility will be higher when there is a difference in the atomic size of the atoms making up the crystal, and (3) the hole mobility will be less in crystals composed of a mixture of atoms.

The first trend, an increase in mobility with crystals of higher atomic weight, can probably be explained by considering the thermal vibrations of the atoms which produce scattering of the current carriers moving through the crystal. The amplitude of these vibrations will be inversely porportional to the atomic weight, but will also depend on the strength of the bonding between atoms which explains departures from this tendency for crystals with very high and very low binding energies.

The second trend, higher electron mobility when there is a difference in the atomic size of the atoms making up the crystal, is probably caused by a greater free space between atoms. This will be particularly true for the larger atoms.

The third trend, decreased hole mobility in crystals composed of a mixture of atoms, is probably the result of local strains produced in the covalent bonds when one atom donates more electrons than the other. These nonuniformities will impede motion of the holes through the crystal.

Crystal Quality. For semiconductor purposes, single crystals are needed: That is, the covalent bonds must be continuous throughout the crystal. Minor defects are produced when atoms are missing from the crystal lattice or when impurities are present. The minority carrier lifetime is extremely sensitive to the number of defects present since recombinations can take place at imperfections in the crystal structure. This represents a major problem with most materials.

Practical Materials. At the present time only germanium and silicon are used in the production of transistors. Their ionization energy is high enough to permit operation at reasonably high temperatures (to about $100^{\circ}C$ for germanium and $200^{\circ}C$ for silicon); and the carrier mobilities are acceptably high. Furthermore, techniques have been developed to produce the high purity crystals necessary in this application. The technology of germanium is somewhat more advanced than silicon with the result that better crystals can be grown from germanium.

Minority carrier lifetime is not so critical in a junction diode; hence, crystals of lower quality can be used. Germanium and silicon are by far the most popular material for the construction of diodes, but diodes with a maximum operating temperature of 500°C have been made from silicon carbide. The performance of these diodes is somewhat poor because of the low carrier mobility in silicon carbide crystals. Gallium arsenide has been used in the construction of tunnel diodes where the minority carrier lifetime is of no significance whatsoever.

Carbon (diamond) is a promising material for very high temperature operation since it has a high ionization energy and respectable carrier mobilities. However, the difficulties encountered in purifying the material and growing high quality crystals have yet to be overcome.