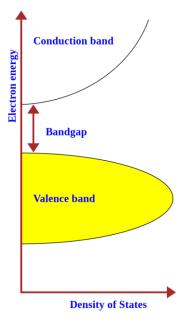
<sup>1</sup>The Periodic Table is one of the useful tools in chemistry. The table was developed around 1869 by Dimitri Mendeleev in Russia and Lothar Meyer in Germany. Both used the chemical and physical properties of the elements and their tables were very similar. In vertical groups of elements known as families we find elements that have the same number of valence electrons such as the Alkali Metals, the Alkaline Earth Metals, the Noble Gases, and the Halogens.

<sup>2</sup>Metals conduct electricity extremely well. Many solids, however, conduct electricity somewhat, but nowhere near as well as metals, which is why such materials are called semiconductors. Two examples of semiconductors are silicon and germanium, which lie immediately below carbon in the periodic table. Like carbon, each of these elements has four valence electrons, just the right number to satisfy the octet rule by forming single covalent bonds with four neighbors. Hence, silicon and germanium, as well as the gray form of tin, crystallize with the same infinite network of covalent bonds as diamond.

<sup>3</sup>The band gap is an intrinsic property of all solids. The following image should serve as good springboard into the discussion of band gaps. This is an atomic view of the bonding inside a solid (in this image, a metal). As we can see, each of the atoms has its own given number of energy levels, or the rings around the nuclei of each of the atoms. These energy levels are positions that electrons can occupy in an atom. In any solid, there are a vast number of atoms, and hence, a vast number of energy levels. In solids, these atoms are packed tightly with one another, and thus, the energy levels of those atoms will be packed tightly onto one another.

A principle necessary to understand the concept of band gaps is the principle of *convergence*. Consider a single atom, for example. Atoms have a given number of energy levels, however, as an atom has more and more energy levels, the spacing between those energy levels *decreases*. Thus, the energy levels of an atom are not evenly spaced like the rungs of a ladder, but instead, have an unequal spacing that decreases as an atom has more and more energy levels.

The prior explanation of convergence only regarded a single atom. However, quite evidently, we understand that there are hundreds of billions of atoms in any solid. All of those energy levels will interact and pack onto one another, forming what are called *bands*. As the number of energy gaps approaches infinity (which is appropriate to consider in the context of a solid), two important energy bands are formed, the *conduction band* and the *valence band*.



<sup>&</sup>lt;sup>1</sup> Adapted from Periodic Properties and Light-Emitting Diodes by Arthur Ellis, Lynn Hunsberger, and George Lisensky in A Materials Science Companion, American Chemical Society 1993.

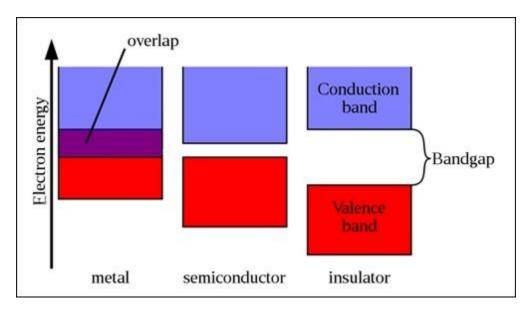
<sup>&</sup>lt;sup>2</sup> Adapted from Brown, LeMay, and Bursten, Chemistry the central science 13<sup>th</sup> edition

<sup>&</sup>lt;sup>3</sup> Adapted from <u>https://www.quora.com/Why-do-semiconductors-have-a-band-gap</u> by Don Li

If you really want to observe how energy bands are formed from the interaction of many energy levels in a solid, run the PhET simulation titled "Band Structures" run by the University of Colorado at Boulder. Watch how the conduction and valence bands are formed as you add more and more atoms (represented as quantum wells) to the simulation. Here is the link: <u>Band</u> <u>Structure</u>

When these two types of bands are produced, there is a space (a certain quantity of energy) between these two bands. **This is the band gap**. This is the region where no electron states can exist (they can only exist in either of the two bands). Simply put, the band gap is the region that separates the valence and conduction bands.

But how might the concept of band gaps apply to how we can define conductors, insulators, and semiconductors? We know that conductors conduct electricity, insulators don't, and that semiconductors normally don't, but can when they are doped with another element and placed in junctions. This following diagram explains the relation between band gaps and classifications of solids.



So what does this diagram demonstrate to us? In the case of a conductor, the valence and conductions band *overlap*. In the case of an insulator, the valence and conduction bands are very far away from one another. Semiconductors, likewise, have a sort of mix between both the band properties of conductors and insulators. The band gap of a semiconductor is small unlike an insulator, but there is no overlapping of bands like in a conductor.

The energy gap, especially in the context of solid-state electronics, represents the amount of energy needed to move electrons across from one band to another. Considering this, this explains why conductors so readily conduct electricity, while insulators don't. Conductors have no band gap, so it is easy for electrons to move from one band to another. Insulators have a large band gap, making it difficult to move electrons from one band to the other.

Semiconductors, when undoped, will not conduct electricity readily because it has a band gap. However, the presence of dopants will increase the conductivity of the semiconductor.

<sup>2</sup>Semiconductors can be divided into two classes, elemental semiconductors, which contain only one type of atom, and compound semiconductors, which contain two or more elements. The elemental semiconductors all come from group 4A. As we move down the periodic table, bond distances increase, which decreases orbital overlap. This decrease in overlap reduces the energy difference between the top of the valence band and the bottom of the conduction band. As a result, the band gap decreases on going from diamond (5.5 eV, an insulator) to silicon (1.11 eV) to germanium (0.67 eV) to gray tin (0.08 eV). In the heaviest group 4A element, lead, the band gap collapses altogether. As a result, lead has the structure and properties of a metal.

Compound semiconductors maintain the same average valence electron count as elemental semiconductors—four per atom. For example, in gallium arsenide, GaAs, each Ga atom contributes three electrons and each As atom contributes five, which averages out to four per atom—the same number as in silicon or germanium. Hence, GaAs is a semiconductor. Other examples are InP, where indium contributes three valence electrons and phosphorus contributes five, and CdTe, where cadmium provides two valence electrons and tellurium contributes six. In both cases, the average is again four valence electrons per atom. GaAs, InP, and CdTe all crystallize with a zinc blende structure.

There is a tendency for the band gap of a compound semiconductor to increase as the difference in group numbers increases. For example, Eg = 0.67 eV in Ge, but Eg = 1.43 eV in GaAs. If we increase the difference in group number to four, as in ZnSe (groups 2B and 6A), the band gap increases to 2.70 eV. This progression is a result of the transition from pure covalent bonding in elemental semiconductors to polar covalent bonding in compound semiconductors. As the difference in electronegativity of the elements increases, the bonding becomes more polar and the band gap increases.

Electrical engineers manipulate both the orbital overlap and the bond polarity to control the band gaps of compound semiconductors for use in a wide range of electrical and optical devices. The band gaps of several elemental and compound semiconductors are given in Table 12.4.

Material	Structure Type	$E_{g'}  \mathrm{eV}^+$					
Si	Diamond	1.11		13	14	15	
AlP	Zinc blende	2.43		Al	Si	Р	
Ge	Diamond	0.67	30	31	32	33	34
GaAs	Zinc blende	1.43	Zn	Ga	Ge	As	Se
ZnSe	Zinc blende	2.58	48	49	50	51	52
CuBr	Zinc blende	3.05	Cd	In	Sn	Sb	Te
Sn‡	Diamond	0.08					
InSb	Zinc blende	0.18					
CdTe	Zinc blende	1.50					

<sup>†</sup> Band gap energies are room temperature values,  $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}.$ 

<sup>‡</sup> These data are for gray tin, the semiconducting allotrope of tin. The other allotrope, white tin, is a metal.

Table 12.4 Band Gaps of Select Elemental and Compound Semiconductors

One of the groups of focus in this experiment is Group 4A or group 14. We will be looking at solids that are contained within LED (light emitting diode) lights. We will think of these as solid solutions behaving as the same valence electron configuration as the metals contained in Group 4A (C, Si, Ge, Sn, and Pb). The strength by which an electron is held in a localized bond also depends on the difference in electronegativity between the atoms (ability to attract electrons to itself, see Figure 8.10 Kotz). The LED lights that we will use all have essentially the same size unit cells (valence electrons) and will behave in a similar manor to their counterparts in Group 4A. As the radius gets smaller the band gap gets larger therefore more voltage will be needed to connect the circuit which lights the LED.

The periodic trends of several metals will also be investigated in this experiment. Magnesium, calcium, and aluminum will be reacted with water and acid to determine trends in metal activity within a group and across a period of the periodic table. Locate each of these metals on the periodic table and identify the group that each belongs to.

See Appendix A for more details on Bonding in metals and Semiconductors and Semiconductors.

#### **Objectives**

- 1. Observe the colors and voltages for Group 4A LED lights
- 2. Calculate the measured wavelength for the LED lights
- 3. Investigate the reactivity order of several metals (which metal is most reactive)

Prior to lab read the sections of our textbook that address periodic trends in atomic radius and the periodic table.

#### PERIODIC PROPERTIES AND LIGHT-EMITTING DIODES Procedure

Obtain a circuit board kit. Ensure that the board looks like Figure 1. Many LED lights look identical so please do not mix them up. Each light is labeled with a colored sticker and a label.

Make sure that the 9V battery is connected to the circuit board. The circuit is "turned on" by inserting the LED into the blue spots on the board, see Figure 2. Plug each LED into the board. For each composition of LED, record the color of light emitted. For each LED light, also record the current in the LED. Set the meter to read DC volts to the nearest 0.01V (i.e. DC 20). Measure the voltage drop across each of the LEDs while it is connected to the board (red lead to the left side of the resistor, the black lead touches the first prong of the LED (bottom blue connection).

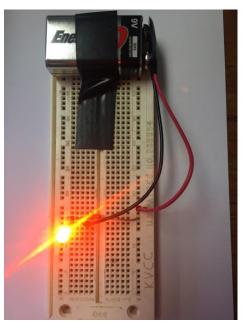


Figure 1. Circuit Board

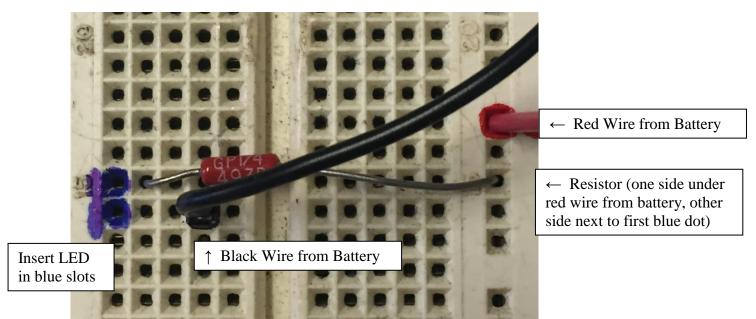


Figure 1. Connections for LED Experiment. Note: if LED does not light up, turn it around. Tall side should be towards the top of the plate (battery side).

Record all of your observations on the excel spreadsheet and answer the questions at the end of the table in Excel. Remember: we will think of these as solid solutions behaving as the same valence electron configuration as the metals contained in Group 4A (C, Si, Ge, Sn, and Pb). The LED lights that we will use all have essentially the same size unit cells (valence electrons) and will behave in a similar manor to their counterparts in Group 4A. As the radius gets smaller the band gap gets larger therefore more voltage will be needed to connect the circuit which lights the LED.

## **REACTIVITY OF METALS**

The purpose of this experiment is to identify periodic trends in the reactivity of metals. The reactions of magnesium, calcium, and aluminum with water and acids will be compared in order to determine the trend in metal activity within a group and across a period in the periodic table.

## Materials:

Aluminum foil	Calcium turnings and Magnesium ribbon
Deionized water	0.5 M Hydrochloric acid
pH paper	Forceps, Spatula, Thermometer

*Caution:* Calcium and magnesium are reactive, flammable solids and possible skin irritants. Use forceps or a spatula to handle these metals.

Hydrochloric acid is corrosive to skin and eyes.

#### **Procedure:**

- 1. In a small weighing tray, place 2 small pieces of calcium turnings. Label this Ca.
- 2. In another tray, place 2 small pieces of magnesium ribbon. Label this Mg.
- 3. Tear off two 1 cm<sup>2</sup> pieces of aluminum foil and roll each into a loose ball. Place the aluminum foil in another tray.
- 4. Place a test plate on top of a sheet of paper with rows labeled A and B and columns labeled 1 3.
- 5. Use an eyedropper to add 20 drops of distilled water to wells A1-A3.
- 6. Test the water in wells A1-A3 with a piece of pH paper and record the initial pH in the data table.
- 7. Use forceps to add one piece of calcium to well A1 and one piece of magnesium ribbon to well A2. Add the aluminum metal to well A3.
- 8. Observe each well and record all immediate observations in the data table. If no changes are observed, write NR (No Reaction) in the data table.
- 9. Re-test the water in wells A1-A3 with a piece of pH paper and record the pH in the data table.
- 10. Continue to watch each well for 1-2 minutes. Record any additional observations, especially comparing the rates of reaction (how quickly each metal reacts).
- 11. Use an eyedropper to add 10 drops of 0.5 M HCl to wells B1-B3. Measure the initial temperature of the solutions in well B1-B3 and record the values in the data table.
- 12. Do ONE metal at a time. Use forceps to add one piece of calcium to well B. Later add one piece of magnesium ribbon to well B2. Tear off a 1 cm<sup>2</sup> piece of aluminum foil and roll it into a loose ball. Add the aluminum metal to well B3.
- 13. Observe each well and record all immediate observations in the data table. If no changes are observed, write NR in the data table.
- 14. Using a thermometer, measure the temperature of each solution in wells B1-B3. Record the final temperature of each solution in the data table.

## Appendix A

## Bonding in metals and Semiconductors (section 12.4 in Kotz)

The melting point of most metals is quite high so we know there must be substantial forces holding them together. The classic description of these structures involves a lattice of metal atoms in a sea of delocalized electrons, and one can visualize that coulombic forces of attraction between the electrons and the charged nuclei provide this force. This model readily explains the electrical conductivity of metals which results because the electrons are free to move with little resistance through the lattice under the influence of an electric potential.

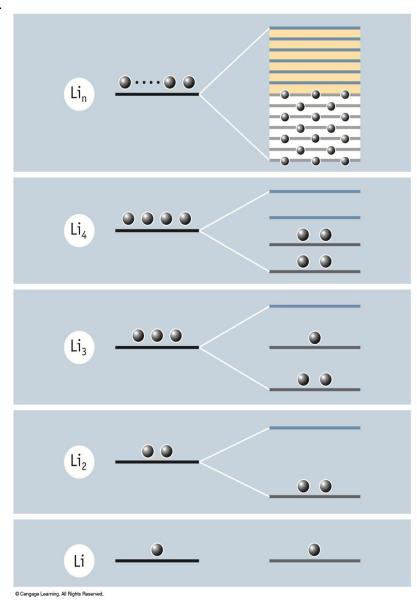
An alternative and more detailed view of metallic bonding is the band model. Recall that molecular orbital theory (Chapter 9) was used to rationalize covalent bonding in molecules. MO theory can be applied to bonding in metals by viewing a metal as a kind of "supermolecule" with an enormous number of atoms.

Even a tiny piece of metal contains a very large number of atoms and an even larger number of valence orbitals. In 1 mol of lithium atoms, for example, there are  $6 \times 10^{23}$  atoms. Considering only the 2s valence orbitals of lithium, there are  $6 \times 10^{23}$  atomic orbitals, from which  $6 \times 10^{23}$  molecular orbitals can be created. (Recall that the total number of molecular orbitals is equal to the total number of atomic orbitals contributed by the combining atoms; Section 9-3. If p and d orbitals are brought into the picture, then many more molecular orbitals are created.) The molecular orbitals that we envision in lithium, or for any metal, will span all the atoms in the crystalline solid. A mole of lithium has 1 mol of valence electrons, and these electrons occupy the lower-energy bonding orbitals. The bonding is described as delocalized because the electrons are associated with all the atoms in the crystal and not with a specific bond between two atoms.

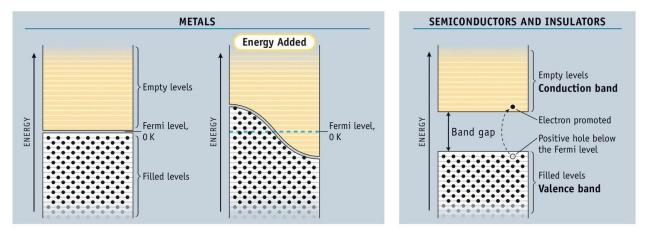
This theory of metallic bonding is called band theory. An energy level diagram would show the bonding and antibonding molecular orbitals blending together into a band of molecular orbitals (Figure 12.13), with the individual MOs being so close together in energy that they are not distinguishable. Each molecular orbital can accommodate two electrons of opposite spin.

In metals, there are not enough electrons to fill all of the molecular orbitals. In 1 mol of Al atoms, for example,  $18 \times 10^{23}$  s and p electrons, or  $9 \times 10^{23}$  electron pairs, are sufficient to fill only a portion of the  $24 \times 10^{23}$  molecular orbitals created by the s and p orbitals of the Al atoms. Many more orbitals are avail- able than electron pairs to occupy them.

Figure 12.13 Bands of molecular orbitals in a lithium crystal. Here, the 2s valence orbitals of Li atoms are combined to form molecular orbitals. As more and more atoms with the same valence orbitals are added, the number of molecular orbitals grows until the orbitals are so close in energy that they merge into a band of molecular orbitals. If 1 mol of Li atoms, each with its 2s valence orbital, is combined,  $6 \times 10^{23}$  molecular orbitals are formed. However, only 1 mol of electrons, or  $3 \times$  $10^{23}$  electron pairs, is available, so only half of these molecular orbitals are filled. (See Section 9-3 in Kotz for the discussion of *molecular orbital theory.*)



At 0 K, the electrons in any metal will all be in orbitals with the lowest possible energy, corresponding to the lowest possible energy for the system. The highest filled level at 0 K is called the Fermi level (Figure 12.14).



**Metals.** The highest filled level at 0 K is referred to as the *Fermi level*. As energy is added as the temperature increases, some electrons now occupy levels above the Fermi level, which depletes levels below the Fermi level.

**Semiconductors.** In contrast to metals, the band of filled levels (the valence band) is separated from the band of empty levels (the conduction band) by a band gap. In insulators, the energy of the band gap is large.

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Figure 12.14 Band theory applied to metals, semiconductors, and insulators. The bonding in metals and semiconductors can be described using molecular orbital theory. Molecular orbitals are constructed from the valence orbitals on each atom and are delocalized over all the atoms.

In metals at temperatures above 0 K, thermal energy will cause some electrons to occupy orbitals above the Fermi level. Even a small input of energy (for example, raising the tempera- ture a few degrees above 0 K) will cause electrons to move from filled orbitals to higher-energy orbitals. For each electron pro- moted, two singly occupied levels result: a negative electron in an orbital above the Fermi level and a positive "hole"—from the absence of an electron—below the Fermi level.

The positive holes and negative electrons in a piece of metal account for its electrical conductivity. Electrical conductivity arises from the movement of electrons and holes in singly occupied states in the presence of an applied electric field. When an electric field is applied to the metal, negative electrons move toward the positive side, and the positive "holes" move to the negative side. (Positive holes "move" be- cause an electron from an adjacent atom can move into the hole, thereby creating a fresh "hole.")

The band of energy levels in a metal is essentially continuous, that is, the energy gaps between levels are extremely small. A consequence of this is that a metal can absorb energy of nearly any wavelength, causing an electron to move to a higher energy state. The now-excited system can immediately emit a photon of the same energy as the electron returns to the original energy level. This rapid and efficient absorption and reemission of light make polished metal surfaces be reflective and appear lustrous (shiny).

This picture for metallic bonding provides an interpretation for other physical characteristics of metals. For example, most metals are malleable and ductile, mean- ing they can be rolled into sheets and drawn into wires. In these processes, the metal atoms must be able to move fairly freely with respect to their nearest neighbors. This is possible because metallic bonding is delocalized—that is, nondirectional. The lay- ers of atoms can slip past one another relatively easily (as if the delocalized electrons were ball bearings that facilitate this motion), while at the

same time the layers are bonded through coulombic attractions between the nuclei and the electrons.

In contrast to metals, rigid network solids such as diamond, silicon, and silica (SiO<sub>2</sub>) have localized bonding, which anchors the component atoms or ions in fixed positions. Movement of atoms in these structures relative to their neighbors requires breaking covalent bonds. As a result, such substances are typically hard and brittle. They will not deform under stress as metals do, but instead tend to cleave along crystal planes.

# Semiconductors (from Brown, LeMay, and Bursten, Chemistry the central science 13<sup>th</sup> edition)

Metals conduct electricity extremely well. Many solids, however, conduct electricity somewhat, but nowhere near as well as metals, which is why such materials are called semiconductors. Two examples of semiconductors are silicon and germanium, which lie immediately below carbon in the periodic table. Like carbon, each of these elements has four valence electrons, just the right number to satisfy the octet rule by forming single covalent bonds with four neighbors. Hence, silicon and germanium, as well as the gray form of tin, crystallize with the same infinite network of covalent bonds as diamond.

When atomic s and p orbitals overlap, they form bonding molecular orbitals and antibonding molecular orbitals. Each pair of s orbitals overlaps to give one bonding and one antibonding molecular orbital, whereas the p orbitals overlap to give three bonding and three antibonding molecular orbitals. (Section 9.8) The extended network of bonds leads to the formation of the same type of bands we saw for metals in Section 12.4. However, unlike metals, in semiconductors an energy gap develops between the filled and empty states, much like the energy gap between bonding and antibonding orbitals. (Section 9.6) The band that forms from bonding molecular orbitals is called the valence band, and the band that forms the antibonding orbitals is called the conduction band (Figure 12.30). In a semiconductor, the valence band is filled with electrons and the conduction band is empty. These two bands are separated by the energy band gap Eg. In the semiconductor community, energies are given in electron volts (eV);  $1 \text{ eV} = 1.602 \times 10-19J$ . Band gaps greater than ~3.5 eV are so large that the material is not a semiconductor; it is an insulator and does not conduct electricity at all.

Semiconductors can be divided into two classes, elemental semiconductors, which contain only one type of atom, and compound semiconductors, which contain two or more elements. The elemental semiconductors all come from group 4A. As we move down the periodic table, bond distances increase, which decreases orbital overlap. This decrease in overlap reduces the energy difference between the top of the valence band and the bottom of the conduction band. As a result, the band gap decreases on going from diamond (5.5 eV, an insulator) to silicon (1.11 eV) to germanium (0.67 eV) to gray tin (0.08 eV). In the heaviest group 4A element, lead, the band gap collapses altogether. As a result, lead has the structure and properties of a metal.

Compound semiconductors maintain the same average valence electron count as elemental semiconductors—four per atom. For example, in gallium arsenide, GaAs, each Ga atom contributes three electrons and each As atom contributes five, which averages out to four per atom—the same number as in silicon or germanium. Hence, GaAs is a semiconductor. Other examples are InP, where indium contributes three valence electrons and phosphorus contributes five, and CdTe, where cadmium provides two valence electrons and tellurium contributes six. In both cases, the average is again four valence electrons per atom. GaAs, InP, and CdTe all crystallize with a zinc blende structure.

There is a tendency for the band gap of a compound semiconductor to increase as the difference in group numbers increases. For example, Eg = 0.67 eV in Ge, but Eg = 1.43 eV in GaAs. If we increase the difference in group number to four, as in ZnSe (groups 2B and 6A), the band gap increases to 2.70 eV. This progression is a result of the transition from pure covalent bonding in elemental semiconductors to polar covalent bonding in compound semiconductors. As the difference in electronegativity of the elements increases, the bonding becomes more polar and the band gap increases.

Electrical engineers manipulate both the orbital overlap and the bond polarity to control the band gaps of compound semiconductors for use in a wide range of electrical and optical devices. The band gaps of several elemental and compound semiconductors are given in Table 12.4.

Material	Structure Type	$E_{g'} eV^{\dagger}$
Si	Diamond	1.11
AlP	Zinc blende	2.43
Ge	Diamond	0.67
GaAs	Zinc blende	1.43
ZnSe	Zinc blende	2.58
CuBr	Zinc blende	3.05
Sn‡	Diamond	0.08
InSb	Zinc blende	0.18
CdTe	Zinc blende	1.50

<sup>+</sup> Band gap energies are room temperature values,  $1 \text{ eV} = 1.602 \times 10^{-19} \text{ J}.$ 

<sup>‡</sup> These data are for gray tin, the semiconducting allotrope of tin. The other allotrope, white tin, is a metal.

Table 12.4 Band Gaps of Select Elemental and Compound Semiconductors

#### Semiconductors (from Kotz)

Semiconducting materials are at the heart of solid-state electronic devices such as computer chips and light-emitting diodes (LEDs) (Figure 12.15). Semiconductors do not conduct electricity easily but can be encouraged to do so by the input of energy. This property allows devices made from semiconductors to essentially have "on" and "off" states, which form the

basis of the binary logic used in computers. We can understand how semiconductors function by looking at their electronic structure, following the band theory approach used for metals.



*Figure 12.15 Electronic devices all made from semiconduc- tors. (top) Computer chip. (left) LED lights. (right) Transistors.* 

Bonding in Semiconductors: The Band gap

The Group 4A elements carbon (an insulator, in the diamond form), silicon, and germanium (semiconductors) have similar structures. Each atom is surrounded by four other atoms at the corners of a tetrahedron (Figure 12.16). Typically, we would represent the bond- ing in these elements using a localized bond model. However, the band model for bonding can also be used with advantage to explain the conductivity of these elements. In the band model, the valence orbitals (the ns and np orbitals) of each atom are combined to form molecular orbitals that are delocalized over the solid. However, unlike metals where there is a continuous band of molecular orbitals, in semiconductors there are two distinct bands, a lower-energy valence band and a higher-energy conduction band, separated by a band gap [Figure 12.14, right, and Figure 12.17]. In the Group 4A elements, the orbitals of the valence band are completely filled and the conduction band is empty. The band gap is an energy barrier to the promotion of electrons from the valence band to the higher-energy conduction band.

The band gap in diamond is 580 kJ/mol—so large that electrons are trapped in the filled valence band and cannot make the transition to the conduction band, even at elevated temperatures. Thus, it is not possible to create positive "holes," and dia- mond is an insulator, a nonconductor.

Silicon and germanium have much smaller band gaps, 106 kJ/mol for silicon and 68 kJ/mol for germanium. As a result they are semiconductors. These elements can conduct a small current because thermal energy is sufficient to promote a few electrons from the valence band across the band gap to the conduction band (Figure 12.17). Conduction then occurs when the electrons in

the conduction band migrate in one direction and the positive holes in the valence band migrate in the opposite direction.

Pure silicon and germanium are called intrinsic semiconductors, with the name referring to the fact that this is an intrinsic or naturally occurring property of the pure material. In intrinsic semiconductors, the number of electrons in the conduc- tion band is determined by the temperature and the magnitude of the band gap. The smaller the band gap, the smaller the energy required to promote a significant num- ber of electrons. As the temperature increases, more electrons are promoted into the conduction band, and a higher conductivity results.

There are also extrinsic semiconductors. The conductivity of these materials is controlled by adding small numbers of different atoms (typically 1 in 106 to 1 in 108) called dopants. That is, the characteristics of semiconductors can be changed by altering their chemical makeup.

Suppose a few silicon atoms in the silicon lattice are replaced by aluminum atoms (or atoms of some other Group 3A element). Aluminum has only three valence elec- trons, whereas silicon has four. Four Si-Al bonds are created per aluminum atom in the lattice, but these bonds must be deficient in electrons. According to band theory, the Si-Al bonds form a discrete but empty band at an energy level higher than the valence band but lower than the conduction band. This level is referred to as an ac- ceptor level because it can accept electrons from the valence band. The gap between the valence band and the acceptor level is usually quite small, so electrons can be promoted readily to the acceptor level. The positive holes created in the valence band are able to move under the influence of an electric potential, so current results from the hole mobility. Because positive holes are created in an aluminum-doped semicon- ductor, this is called a p-type semiconductor (Figure 12.17b, left).

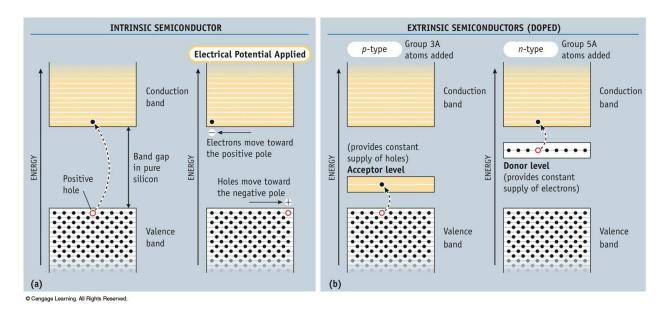


Figure 12.17 Intrinsic (a) and extrinsic (b) semiconductors.

Now suppose phosphorus atoms (or atoms of some other Group 5A element such as arsenic) are incorporated into the silicon lattice instead of aluminum atoms. This material is also a semiconductor, but it now has extra electrons because each phosphorus atom has one more valence electron than the silicon atom it replaces in the lattice. Semiconductors doped in this manner have a discrete, partially filled donor level that resides just below the conduction band. Electrons can be promoted to the conduction band from this donor band, and electrons in the conduction band carry the charge. Such a material, consisting of negative charge carriers, is called an n-type semiconductor (Figure 12.17b, right).

One group of materials that have desirable semiconducting properties is the III-V semiconductors, so called because they are formed by combining elements from Group 3A (such as Ga and In) with elements from Group 5A (such as As or Sb).

Gallium arsenide, GaAs, is a common semiconducting material that has electri- cal conductivity properties that are sometimes preferable to those of pure silicon or germanium. The crystal structure of GaAs is similar to that of diamond and silicon; each Ga atom is tetrahedrally coordinated to four As atoms, and vice versa.

It is also possible for Group 2B and 6A elements to form semiconducting com- pounds such as cadmium sulfide, CdS. The farther apart the elements are found in the periodic table, however, the more ionic the bonding becomes. As the ionic char- acter of the bonding increases, the band gap will increase, and the material will become a weaker semiconductor. Thus, the band gap in CdS is 232 kJ/mol, com- pared to a band gap in GaAs of 140 kJ/mol.

These materials can also be modified by substituting other atoms into the structure. For example, in one widely used semiconductor, aluminum atoms are substituted for gallium atoms in GaAs, giving materials with a range of compositions (Ga1–xAlxAs). The importance of this modification is that the band gap de- pends on the relative proportions of the elements, so it is possible to control the size of the band gap by adjusting the stoichiometry. As Al atoms are substituted for Ga atoms, for example, the band gap energy increases. This consideration is important for the specific uses of these materials in devices such as LEDs (light- emitting diodes).