

Bonds, Bands, and Doping: How Do LEDs Work?

Periodic Trends Experiment

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Key Concepts:

- Bonding in Elemental Solids
 - Metals: Weak Covalent Bonding
 - Nonmetals: Strong Covalent Bonding
 - Periodic Trends in Bonding Properties of Solids
 - Bands and the Conductivity Properties of the Elements
 - Conductivity Properties of the Elements
 - Doping
 - Light-Emitting Diodes (Note: This section includes an animation.)
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Light-Emitting Diodes: Diverse Applications

Light-emitting diodes (LEDs) (Figure 1) are found in so many objects that we use every day that we barely take any notice of them. The digital display (i.e., the bars and dots that make up the numbers) on your alarm clock, the tiny light that indicates whether your iron or computer or electric razor is on, the newer scanners on grocery-store checkout counters, and the red lights on the back of some children's tennis shoes that flash when the child takes a step are everyday examples of LEDs. Pocket laser pointers and the lasers used to scan CD's are also based on LED technology. (Lasers have LEDs in combination with

optical devices (e.g., mirrors) to give a specially directed beam of light.) Although they are now commonplace, LEDs that give off visible light were actually invented relatively recently. In 1962, Nick Holonyak, Jr., while working for General Electric, discovered that the chemical composition of earlier diodes could be changed to make them give off visible light for use in digital displays and indicators. LEDs operate by a completely different mechanism from other sources of light, such as light bulbs and the sun. Furthermore, LEDs release only one particular color of light, and they produce very little heat. In contrast, the "white" light produced by a light bulb or the sun is really a blend of many different colors, and these sources also typically produce a large amount of heat. Hence, LEDs are much more efficient for producing small quantities of light of a particular color than other light sources. Because of this efficiency, scientists and engineers are hard at work to develop designs that will allow LEDs to be used for many new applications, from traffic lights to atmospheric-haze detectors. It has been estimated that replacing all the incandescent traffic lights in the United States with LED traffic signals would save almost 2.5 billion kilowatt hours (roughly equivalent to \$200 million, or 5 billion pounds of CO₂ (from burning fossil fuels to make electricity) released into the atmosphere) per year!

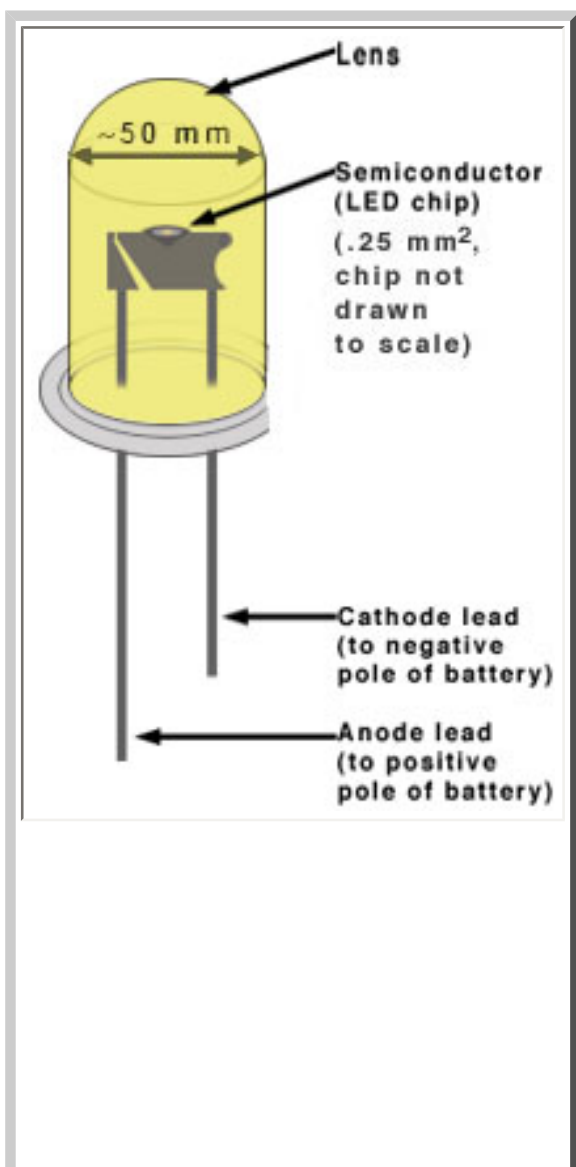


Figure 1

This diagram shows the principal components of a typical LED, such as the one you used in the Experiment to test conductivity. The plastic lens encapsulating the LED takes up most of the space in this device, while the actual LED chip is only about 0.25 mm^2 .

Just what, then, is a light-emitting diode? LEDs are semiconductor devices that can convert electrical energy directly into light, due to the nature of the bonding that occurs in the semiconductor solid. As we shall see, the type of bonding in a solid is directly related to the conductivity of the solid. Metals, nonmetals, and semimetals have different bonding properties that lead to the differences in conductivity that can be observed between these categories of elements. LEDs rely on special conductivity properties in order to emit light. Hence, to understand LEDs we must first look at bonding in elemental solids.

Bonding in Elemental Solids

In the introduction to the Experiment, you learned that metals are electrically conducting because their valence electrons (the outermost electrons of an atom) "swim" in an electron "sea". This picture is useful for imagining how metals have sufficiently mobile charged particles to conduct electricity, but it does not fully explain the difference in conductivity among the various elements. To explain the difference in the properties of metals, semimetals, and nonmetals, and hence to understand how LEDs work, we need to understand the bonding of solids in more detail. Throughout this course (and science, in general), different models (theories) are used to describe a phenomenon (e.g., electrical conductivity). It is important to remember that all models are approximations and will fail at some point, but all have their own usefulness and advantages in describing a phenomenon of interest.

You read in the introduction to the Experiment that the electronegativity of elements increases from the left side of the periodic table (metallic elements) to the right side (nonmetallic elements). (Electronegativity is the ability of an atom in a compound to attract electrons to itself (away from its neighbor).) Because atoms with low electronegativity (i.e., metals) do not hold their valence electrons tightly, their valence-electron orbitals are diffuse and may extend to large distances away from the nucleus. Highly electronegative atoms (i.e., nonmetals) do hold their electrons tightly, and so their valence-electron orbitals are less diffuse and smaller. (To help visualize how high electronegativity makes orbitals

less diffuse and smaller, think of a dog on a leash: if you pull harder on the leash, you bring the dog closer to you, so that its movement is restricted to a smaller area.)

When atoms interact together, their valence orbitals overlap to form **bonds** between the atoms. You have already learned from the Experiment that electronegativity differences are very important in determining the types of bonds that form between atoms of different elements. Electronegativity also plays an important role in determining the properties of bonds between atoms of the same element in a solid (for which, of course, the difference in electronegativity is zero). How can electronegativity help us to understand the behavior of metals, semimetals, and nonmetals?

Metals: Weak Covalent Bonding (Metallic Bonding)

Let us first consider the example of sodium (Na). Na has one valence electron, which is in the 3s orbital. When two Na atoms bond to form a gaseous Na_2 molecule, the two valence electrons (one from each Na atom) are found primarily between the two Na nuclei. To make a crystalline solid, many atoms are packed together in a regular pattern. In metal solids (Figure 2a), the atoms adopt a "closest packed" configuration, in which the atoms are equally spaced, and space between the atoms is minimized. Electrons in diffuse orbitals are not tightly constrained to a small space, and hence the interactions between one Na atom and an adjacent Na atom, or "nearest neighbor," are weak. At the same time, each atom in a metallic solid has many (up to 12) "nearest neighbors," i.e., each atom interacts with many other atoms. Thus, although the individual interactions between atoms are weak, there are many interactions, and the aggregate effect is a well-bonded metallic solid. (To illustrate this point, think of how a woven cloth is held together. Although the individual threads may be quite weak, when many threads are woven together, they form a strong cloth.)

a.

b.

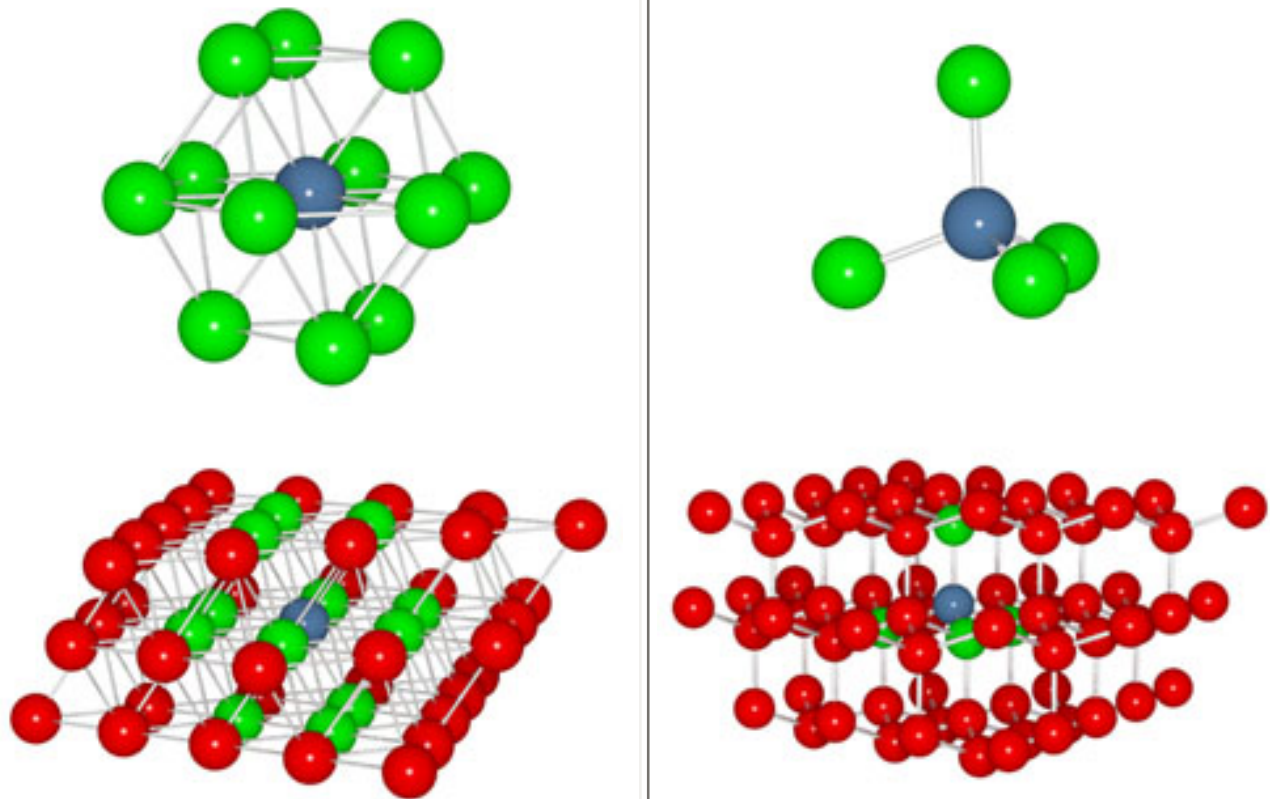


Figure 2

a. This is a representation of the three-dimensional structure of a crystalline metal, in which each atom has 12 nearest neighbors (closest-packed configuration). The bonding in this structure is described above in the section, "Metals: Weak Covalent Bonding."

b. This is a representation of the three-dimensional structure of a crystalline nonmetal, in which each atom has only 4 nearest neighbors. The bonding in this structure is described below in the section, "Nonmetals: Strong Covalent Bonding."

Note: The crystal structures were drawn using PowderCell for Windows, and the images were rendered using POV-Ray (see [References](#)).

The large number of nearest neighbors for metal atoms in a solid effectively causes the atoms to be surrounded in all directions by other atoms' valence-electron orbitals. Recall that when atoms are packed in a solid and interact, their valence orbitals overlap. Thus, in a metallic solid such as sodium, each atom's valence orbital can overlap with many other valence orbitals, in virtually all directions. Each Na atom is affected (perturbed) by its many neighbors and therefore, the valence atomic orbitals of all of the Na atoms "mix" to form an almost continuous **band** of orbitals that are very close in energy. Because these valence atomic orbitals have lost their individual identity in this aggregate of Na atoms, the band formed is called the valence band (Figure 3). (You may find it helpful to think about

what happens to the individual identities of voters in an election. Going into the voting booth, each voter decides for himself or herself how to vote, just as a solitary atom has its own valence orbitals with a certain number of electrons. However, when the results are tallied, the individual identities of the voters are lost; the voters are simply divided into those who voted for one candidate and those who voted for the other candidate. Similarly, when many atoms bond together, the individual identities of the orbitals are lost; they form continuous bands that are divided into the filled and unfilled orbitals.)

The low-electronegative metal atoms "give up" their valence electrons, allowing them to be found throughout the "mixed" orbitals of the valence band. Hence, the band of orbitals is filled to a certain energy according to the number of valence electrons provided by all of the Na atoms in the solid. Because electrons are shared among atoms in these "mixed" orbitals, they form covalent bonds between the atoms in the solid. Each atom shares electrons with all its many neighbors in all directions, so these bonds are **weak covalent bonds**. Because the orbitals are large and diffuse, the bonds they form do not have significant directional preferences. Another term frequently used to describe this type of bonding is "**metallic bonding**," because solids with this type of bonding exhibit metallic properties and are therefore categorized as metals. As we shall see later in the tutorial, elements with metallic bonding are very good conductors of electricity, because of the nondirectionality of the orbitals (i.e., electrons can easily move in any direction). Metallic elements are not used in LEDs, although they are important components of the circuits used to power LEDs.

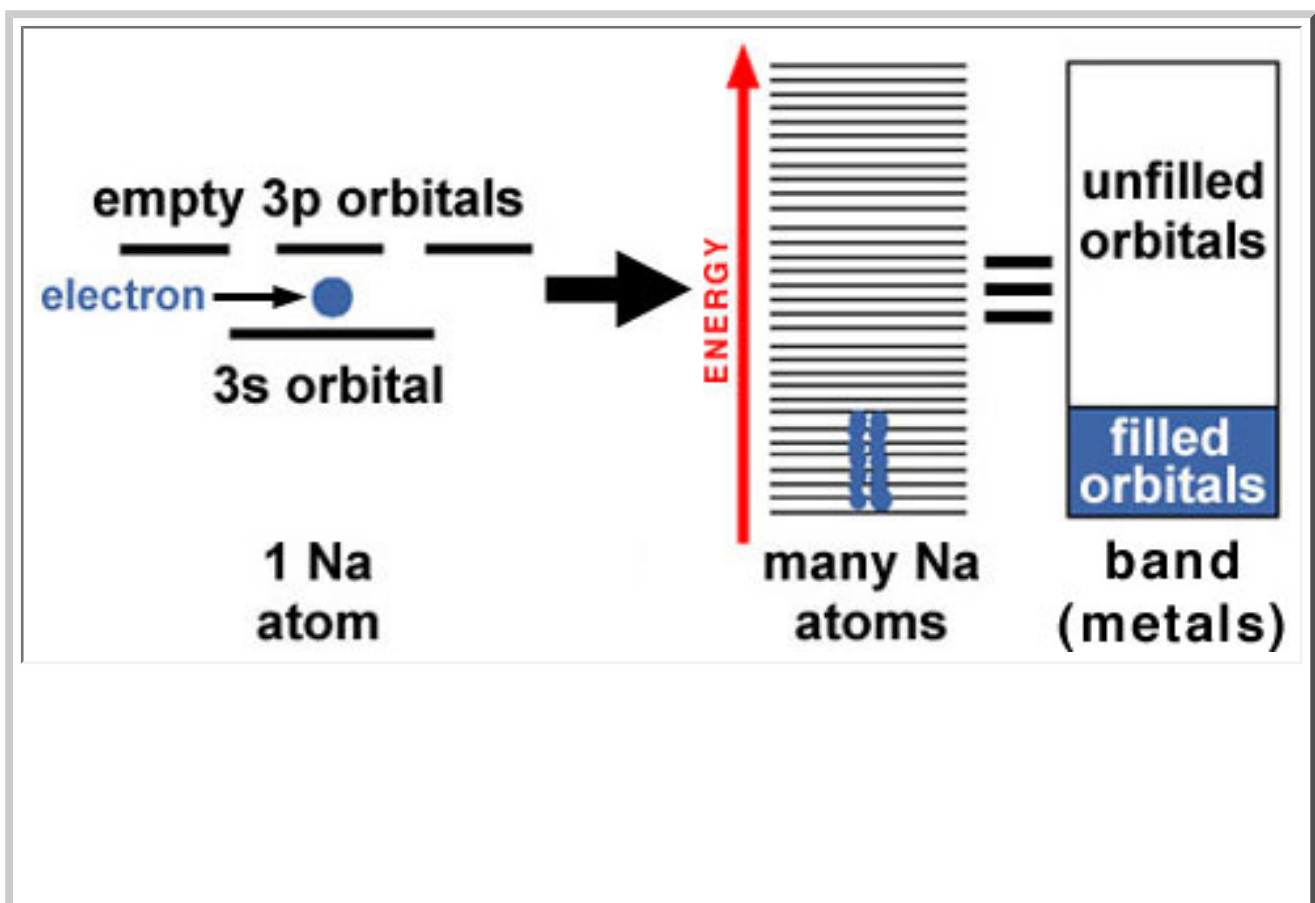


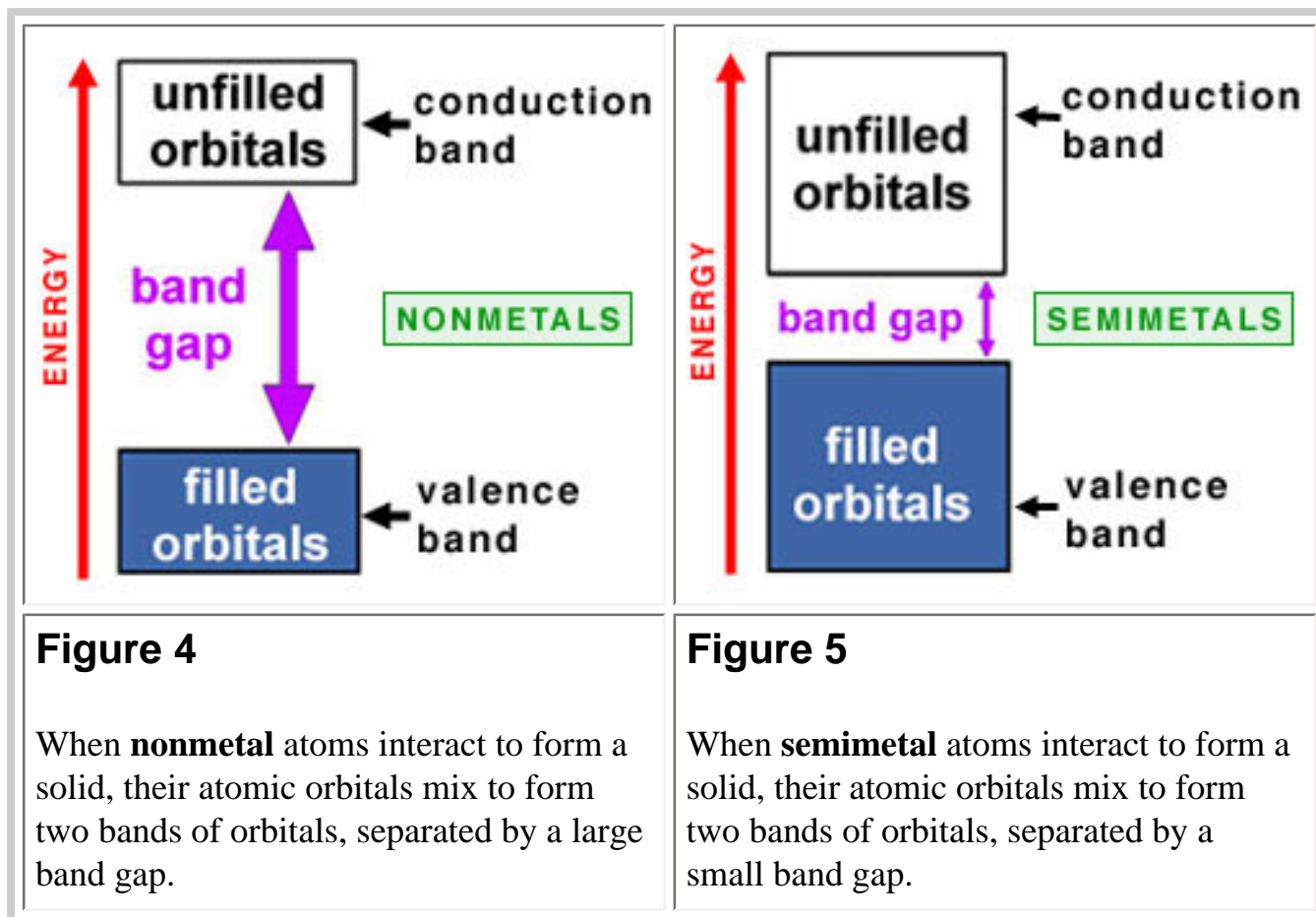
Figure 3

When **metal** atoms interact together to form a solid, their atomic orbitals mix to form a continuous band of orbitals. In the representation of 1 Na atom (left-hand side of diagram), the blue dot represents an electron in the 3s orbital; in the representation of many Na atoms (center of diagram), the blue dots again represent electrons in the "mixed" orbitals that are formed when many atoms interact. This "mixing" of orbitals is better represented by a "band" of orbitals (right-hand side of diagram), in which the blue area represents orbitals that are filled with electrons.

Nonmetals: Strong Covalent Bonding

Now consider the example of carbon (C), a nonmetal. Its electronegativity is high, relative to that of sodium. Therefore, the valence orbitals of a C atom are not diffuse and are smaller than those of Na. When C atoms are packed together to make a solid, the valence orbitals overlap within a small volume, and so the electrons in these orbitals are constrained to a small space. Some of the C atoms are drawn closer together, pulling them further away from others; thus severely distorting the closest-packed structure (Figure 2a) to a nonmetallic crystalline solid structure (Figure 2b). In order to form the nonmetallic solid structure, the highly electronegative atoms interact with only a few (usually four or less) nearest neighbors, and each valence orbital is oriented in the direction of the atom with whose valence orbital it overlaps. Hence, the interactions between those atoms that are drawn close together are strong. As in metal solids, the valence atomic orbitals lose their individual identity in the aggregate of C atoms, and "mix" to form a band of orbitals that are close in energy.

Electrons are shared between atoms in these "mixed" orbitals, but the bonds are directional. Therefore, the bonds formed in nonmetal elemental solids are stronger and are called **strong covalent bonds**. In strong covalent bonds, a large energy gap arises between the orbitals that are formed, as you will see later in Chem 111. When many strong covalent bonds are present, as in the nonmetallic solid, two bands of "mixed orbitals" form, separated by an energy gap called the **band gap** (Figure 4). The lower-energy band consists of filled orbitals (i.e., orbitals containing electrons) and is known as the "valence band"; the higher-energy band consists of unfilled orbitals and is known as the "conduction band". As you go across the periodic table, the band gap increases (as the electronegativity increases). Semimetals (Figure 5), which lie between metals and nonmetals on the periodic table, have an energy gap between the valence and conduction bands (band gap) similar to nonmetals (not a continuous band like metals), but the band gap for semimetals is smaller than for nonmetals.



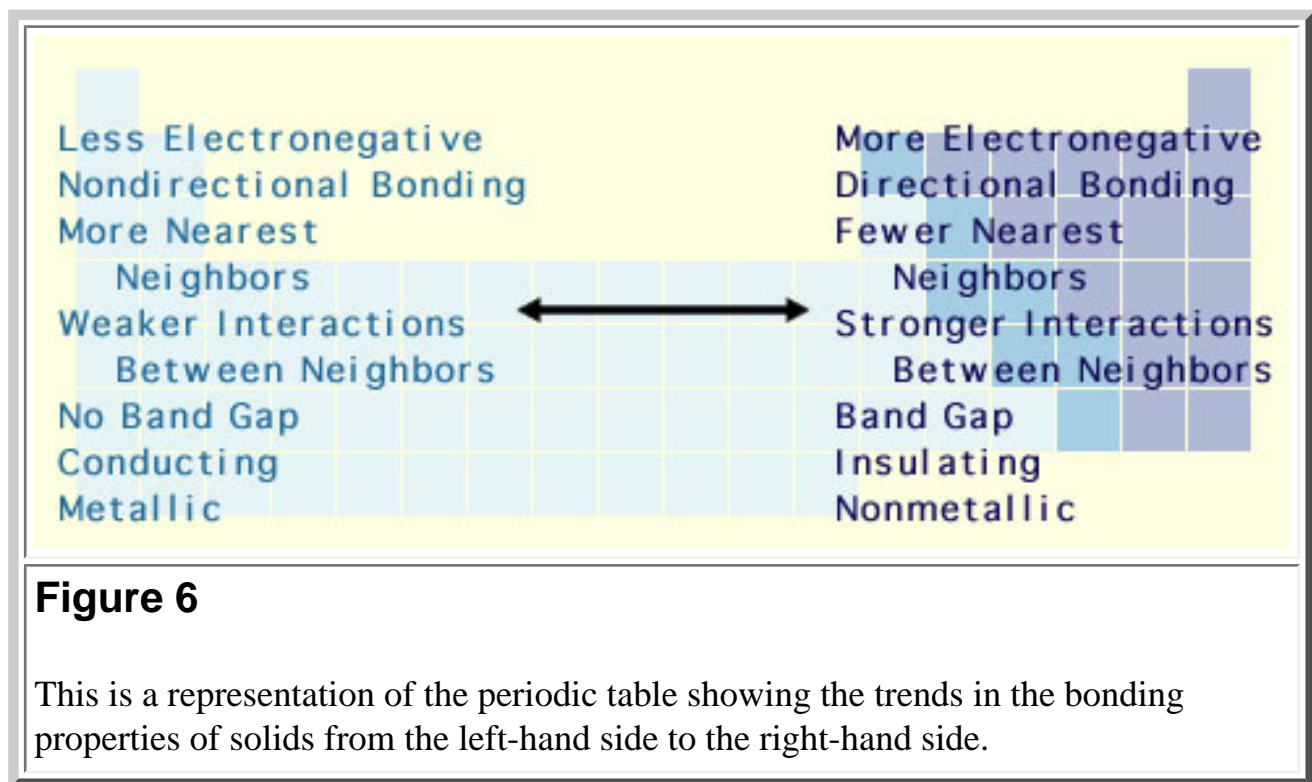
As we shall see later in the tutorial, elements with band gaps are less able to conduct electricity. (Recall that the metals described above are good conductors because they have no band gap.) As the size of the gap increases, the materials become better insulators (poorer conductors of electricity). Hence, nonmetals are usually classified as insulators. It is the semimetals that are used in LEDs. Why are semimetals, and not metals (good conductors) or nonmetals (insulators), used in LEDs? To answer this question, we need to discuss conductivity in terms of bonds. Before we discuss conductivity, we need to summarize the periodic trends described above.

Questions on Bonding in Elemental Solids

- Why is electronegativity related to band gap size and directionality of bonds?
 - Which element would you expect to have a larger band gap in the elemental solid, aluminum (Al) or sulfur (S)? Briefly, explain your reasoning.
-

Summary of Periodic Trends in Bonding Properties of Solids

Figure 6 summarizes the bonding properties of the elemental solids described above. As you can see, the bonding properties of these elemental solids follow particular trends across the periodic table. The less electronegative, metallic elements on the left of the table exhibit weak, nondirectional covalent bonding and no band gap. The more electronegative, nonmetallic elements on the right of the periodic table exhibit strong, directional covalent bonding and a large band gap. Semimetals, which occupy intermediate positions on the periodic table, have bonds of intermediate strength and directionality, and a small band gap. These periodic trends in bonding properties across a row of the periodic table derive from the electronegativities of the atoms. The relative electronegativities in turn are governed in part by the trends in the number of valence electrons that the atom holds.



These periodic trends in bonding properties are also related to the conductivity of the elements. The metals (on the left of the periodic table) tend to be good conductors of electricity, while the nonmetals (on the right of the periodic table) tend to be poor electrical conductors. The semimetals are typically classified as semiconductors, because they conduct electricity, but not as efficiently as the metals. Recall from the discussion of LEDs above that LEDs are semiconductor devices whose light-emitting properties are dependent on the nature of the bonding in the semiconductor. Hence, the next step in understanding how LEDs work is to describe the relationship between bonding (and the bands that form when the atoms are bonded together) and the conductivity properties of the elements.

Bands and the Conductivity Properties of the Elements

Recall from the introduction to the Experiment that substances conduct electricity if they contain mobile charged particles (i.e., ions or electrons). In a solid, electrons can become mobile if the electrons can be promoted to unfilled orbitals in the conduction band of the solid. How can we account for the electrical conductivity of **metals**? Think again about an individual Na atom, containing only one valence electron in the 3s orbital (recall Figure 3). This atom has a half-filled 3s orbital (because the 3s orbital can hold up to 2 electrons) and three unfilled 3p orbitals, as you will learn later in Chem 111. All of these are valence orbitals and combine with those from other atoms in the solid to form the band of "mixed" orbitals described above. However, the number of electrons contained in the valence band is much smaller than the number it is capable of containing. The reason the band is filled much less than its capacity is that each atom contributes only one electron to the band, but contributes four orbitals to the band; hence, the band is capable of holding up to eight electrons per atom. The filled and unfilled portions of the band are continuous (recall Figure 3); **no band gap** is present like in carbon and other nonmetal solids. Therefore, electrons can easily (i.e. with very little energy input) be promoted from filled orbitals in the band to unfilled orbitals in the band, and hence move throughout the metal solid. Therefore, **metals conduct electricity** because the partially-filled band of orbitals allows electrons to move easily throughout the sample.

What about **nonmetals**? We know that nonmetallic solids form two distinct bands. The lower-energy band, known as the valence band, contains all of the valence electrons (the band is filled with electrons), while the higher-energy band, the conduction band, contains no electrons (recall Figure 4). Electrons in the filled valence band cannot move to other orbitals within the band, because all of the orbitals are already filled. No motion of electrons occurs in the conduction band, because it is empty. Now, recall that these bands are separated by a **large band gap**. Therefore, a large amount of input energy is required to promote an electron from the filled lower-energy (valence) band to the unfilled higher-energy (conduction) band. Thus, without the high-energy input to promote an electron from the lower-energy band to the higher-energy band, there are no mobile charge carriers, and the **nonmetallic solid cannot conduct electricity**.

As you should observe in lab, **semimetals** such as silicon (Si) have intermediate properties between those of metals and nonmetals. The band gap in semimetals is small enough (recall Figure 5) that an electron can be promoted from the filled lower-energy band to the unfilled higher-energy band with a moderate input of energy (such as the thermal energy that dissipates in the solid when electrical current is passed through it). Then, the lower-energy (valence) band is no longer completely filled and the higher-energy (conduction) band is no longer completely empty; i.e., both bands are partially filled (Figure 7). In the valence band, electrons can move between orbitals (and thus throughout the solid) once some of the orbitals have become vacant. Promotion of electrons to the conduction band

allows them to move easily between the band's many empty orbitals. Hence, **semimetals can conduct electricity** with a moderate input of energy.

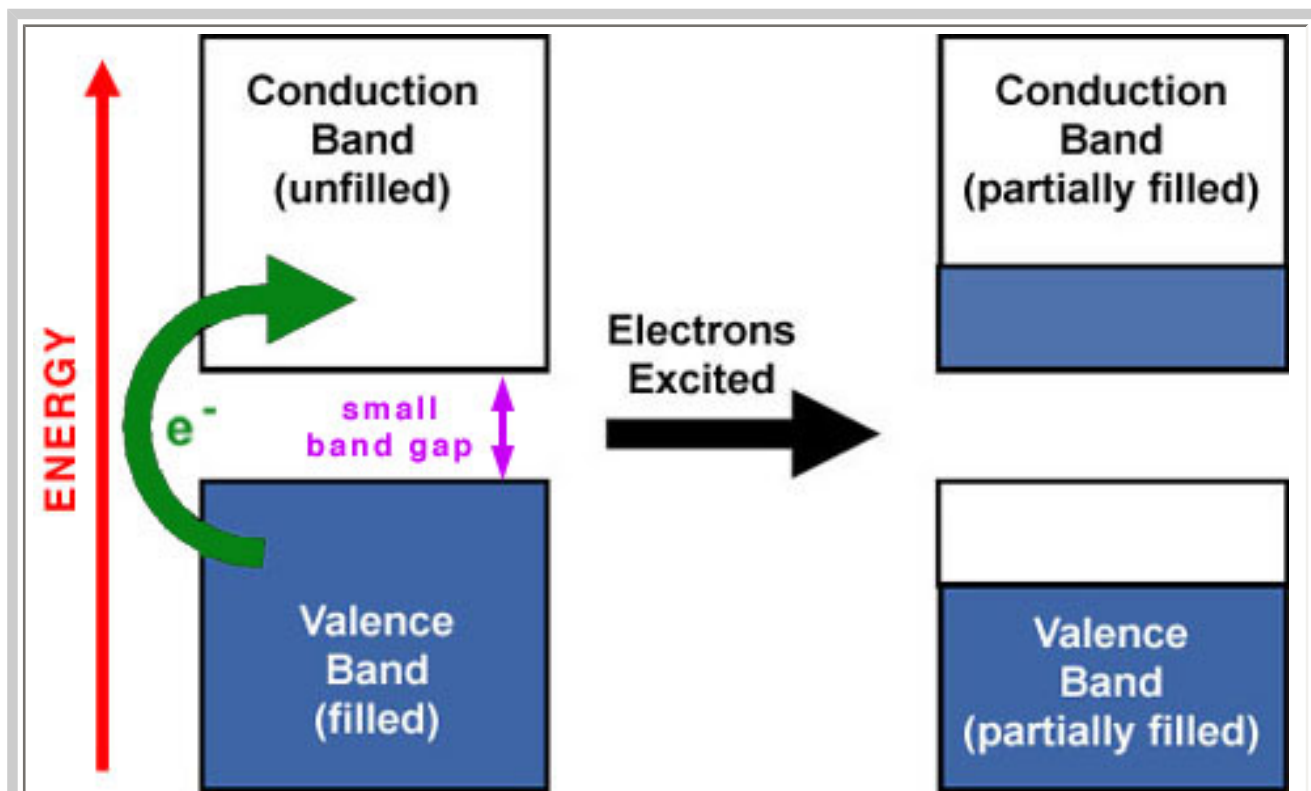


Figure 7

In a semiconductor, the band gap is small enough that electrons can be moved from the orbitals in the valence band to the orbitals in the conduction band. This leaves both bands partially filled, so the material can conduct electricity.

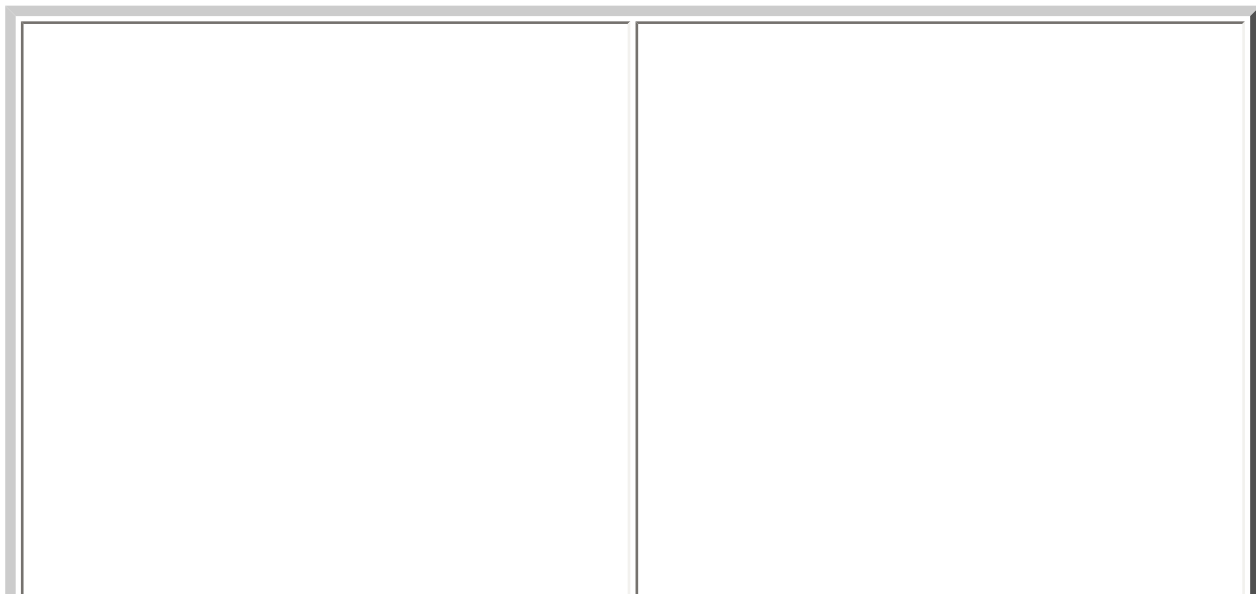
Questions on Bands and the Conductivity Properties of the Elements

- Which would you expect to be a better insulator, bromine (Br) or iodine (I)? Briefly, explain your reasoning.
- A scientist measures the conductivity of solid beryllium (Be), boron (B), and carbon (C). The scientist finds that beryllium is the best conductor, boron conducts electricity slightly, and carbon conducts very little electricity. Briefly, explain the observed differences in conductivity between these elements **in terms of bands and the movement of electrons**.

Doping to Enhance Conductivity of Semiconductors

LEDs are made of semiconductors, but the conductivity of the semiconductors in LEDs has been specially enhanced to allow for the unique properties of LEDs. The conductivity of semiconductors like Si can be increased by adding small, controlled amounts of "impurities" that have roughly the same atomic size, but more or fewer valence electrons than the semimetal. This process is known as **doping**. An impurity with fewer valence electrons (such as Al; see the periodic table) takes up space in the solid structure, but contributes fewer electrons to the valence band, thus generating an electron deficit (Figure 8). This type of dopant creates a space (or "hole") in the lower-energy (valence) band, making room for electrons to travel. Hence, the electrons in the valence band can move from one orbital to another within this band with a small input of energy (smaller than required for the semiconductor without the doping), and thus move throughout the solid. Alternately, an impurity with more valence electrons (such as P; see the periodic table) contributes extra electrons to the band (Figure 9). Since the valence band is already filled by the semimetal, the extra electrons must go into the higher-energy (conduction) band. These electrons now occupy a partially-filled band (the conduction band), can move easily between the orbitals of this band, and thus move easily throughout the solid. Semiconductors whose conductivity has been enhanced with valence-electron-deficient dopants are known as **p-type** semiconductors (*p* for "positive", because it is deficient in negatively-charged electrons), and semiconductors whose conductivity has been enhanced with valence-electron-enriched dopants are known as **n-type** semiconductors (*n* for "negative", because it is enriched with negatively-charged electrons).

Now we know that LEDs are doped semiconductors, and hence conduct electricity with a small input of energy (i.e., LEDs are very efficient). However, we have not yet answered the questions, how does an LED give off light, and why does an LED give off only one specific color of light?



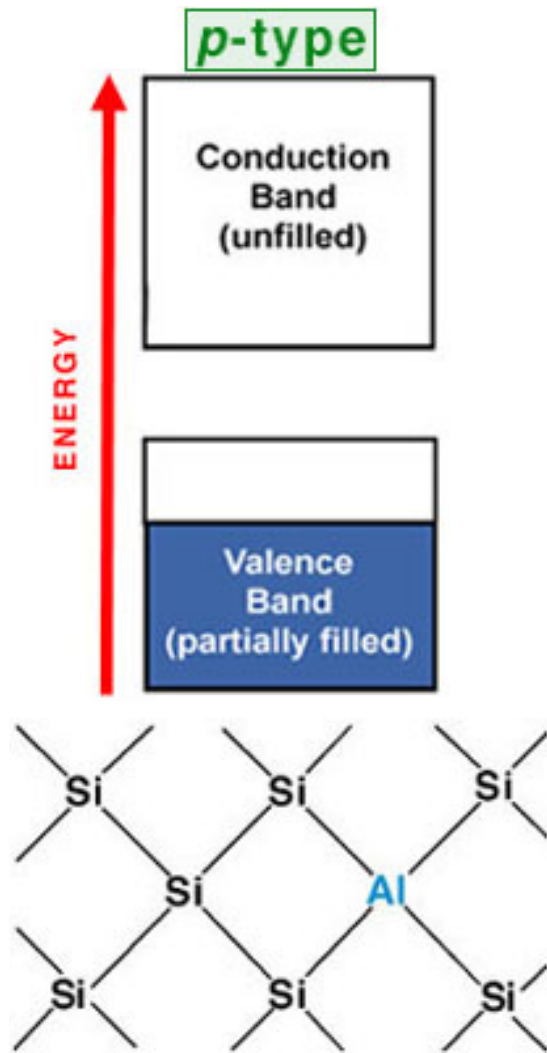


Figure 8

A schematic diagram showing the solid crystal-lattice structure and bands for silicon doped with aluminum, a **p-type semiconductor**.

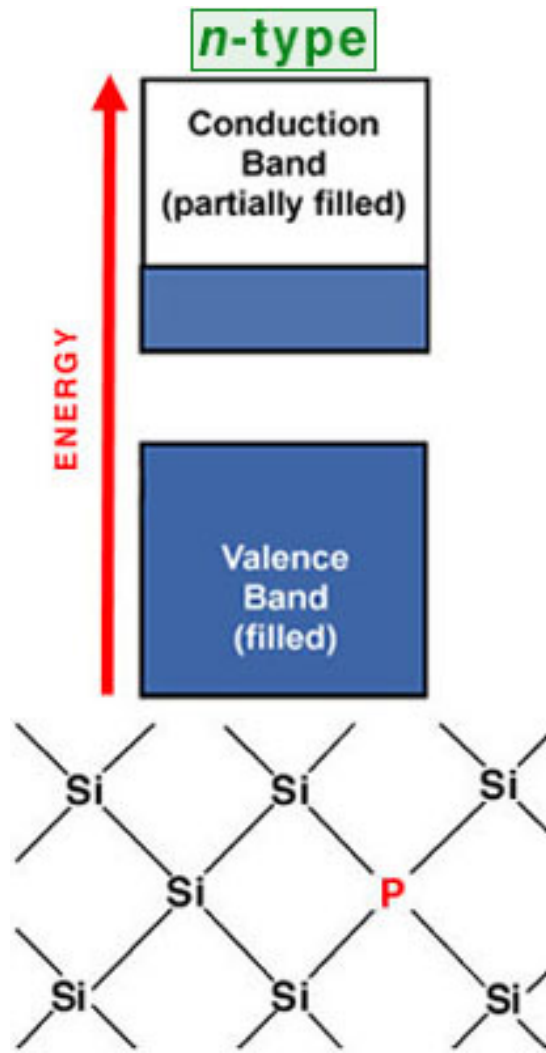


Figure 9

A schematic diagram showing the solid crystal-lattice structure and bands for silicon doped with phosphorus, an **n-type semiconductor**.

Questions on Doping to Enhance Conductivity of Semiconductors

- State whether each of the following could be used to dope arsenic (As): gallium (Ga), phosphorus (P) and selenium (Se). Explain your answer.
- For each of the elements listed above that could be used to dope arsenic, state whether an n-type or p-type semiconductor is formed. Explain your answer..

How Do LEDs Emit Light?

In order to convert electrical current into light, an LED must have a *p*-type semiconductor in contact with an *n*-type semiconductor. This combination of the two types of semiconductors is known as a ***p-n* junction**, or a **diode**. When a *p-n* junction is placed in a circuit with an external power source (e.g., a 9 V battery), electrons from the power source flow to the diode and change the arrangement of electrons in the diode (Figure 10). How does this lead to the emission of light in the LEDs used to test conductivity in this experiment?

Recall that the *p*-type semiconductor (Figure 8) has extra space for electrons in its valence band, and no electrons in its conduction band, while the *n*-type semiconductor (Figure 9) has a full valence band (no space) and extra electrons in its conduction band. If the circuit is constructed such that electrons flow into the *n*-type side of the *p-n* junction from the power source (Figure 10), they will occupy the conduction band, since there is no space in the valence band of an *n*-type semiconductor. As electrons continue to come into the conduction band, they will be pushed to the *p*-type side of the *p-n* junction, which has more space to hold electrons (you can think of the "positive" side attracting the negatively-charged electrons). The electrons go into the empty conduction band of the *p*-type side, since they already occupy the higher-energy band in the *n*-type side. However, once the electrons are in the higher-energy band of the *p*-type side, they will fall to the lower-energy band if there is space available for the electrons to occupy in the valence band. Electrons falling from the higher-energy band of orbitals (conduction band) to the lower-energy band of orbitals (valence band) in the *p*-type semiconductor results in the atoms going from a higher-energy state to a lower-energy state (i.e., becoming more stable). As the electrons cross the band gap, energy related in magnitude to the size of the band gap is released in the form of light.

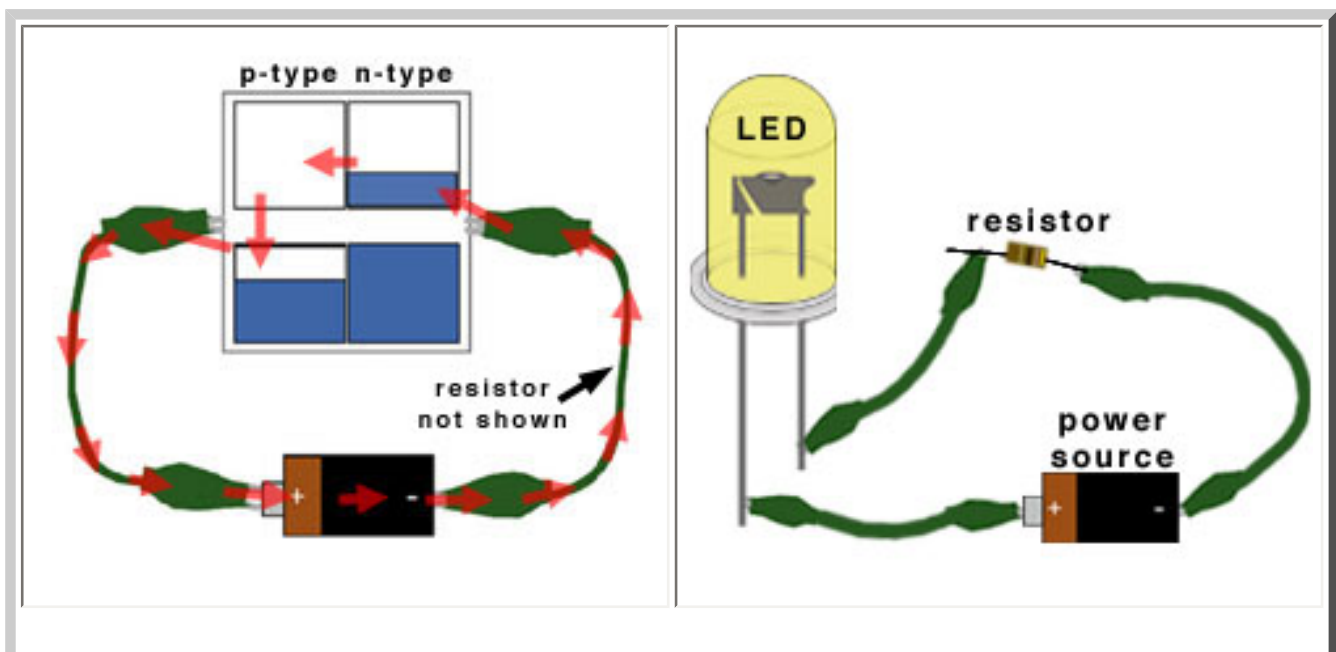


Figure 10

The diagram on the left schematically shows the path of electrons moving through a circuit containing a p - n junction. Electrons flow from the negative (shown in black) pole of the battery to the n -type semiconductor, where they occupy the higher-energy (conduction) band. The electrons then move into the conduction band of the p -type semiconductor and fall into the empty orbitals of the valence band, which releases energy in the form of light. The electrons then move through the wire back to the positive pole (shown in copper) of the battery, and re-circulate. (**Note:** This picture has been simplified to follow the discussion presented here. A more complete picture would show the two doped semiconductors in equilibrium, in which the band gaps are "bent" and a potential energy barrier to electrons moving from the n -type to the p -type semiconductor must be overcome (using the voltage from the battery; known as "biasing"). For more information on bending in diodes, see Ellis *et. al* in the [References](#).)

The diagram on the right depicts a circuit composed of an LED, a resistor, and a power source (battery). The flow of electrons through this circuit is the same as that described above. The resistor in the circuit (which is not shown on the left for ease of viewing) is necessary to limit the current so that the LED does not "burn out" by receiving too much current from the battery.

Please click on the pink button below to view a QuickTime movie showing the flow of electrons through the circuit, and the light emitted by the LED. Click the blue button below to download [QuickTime 6](#) to view the movie.

The color of the light emitted depends on the size of the band gap. The LEDs used in the Experiment are made of a combination of semiconducting materials specially chosen to have the right size band gap for yellow light to be emitted. LEDs that emit red light, which are used in many digital alarm clocks, have a different-size band gap, and therefore a different amount of energy is released in the form of light (Figure 11). (Later in the semester you will learn that light of different colors has different energies.) LEDs that emit infrared rather than visible light are common in remote controls for televisions and stereos.

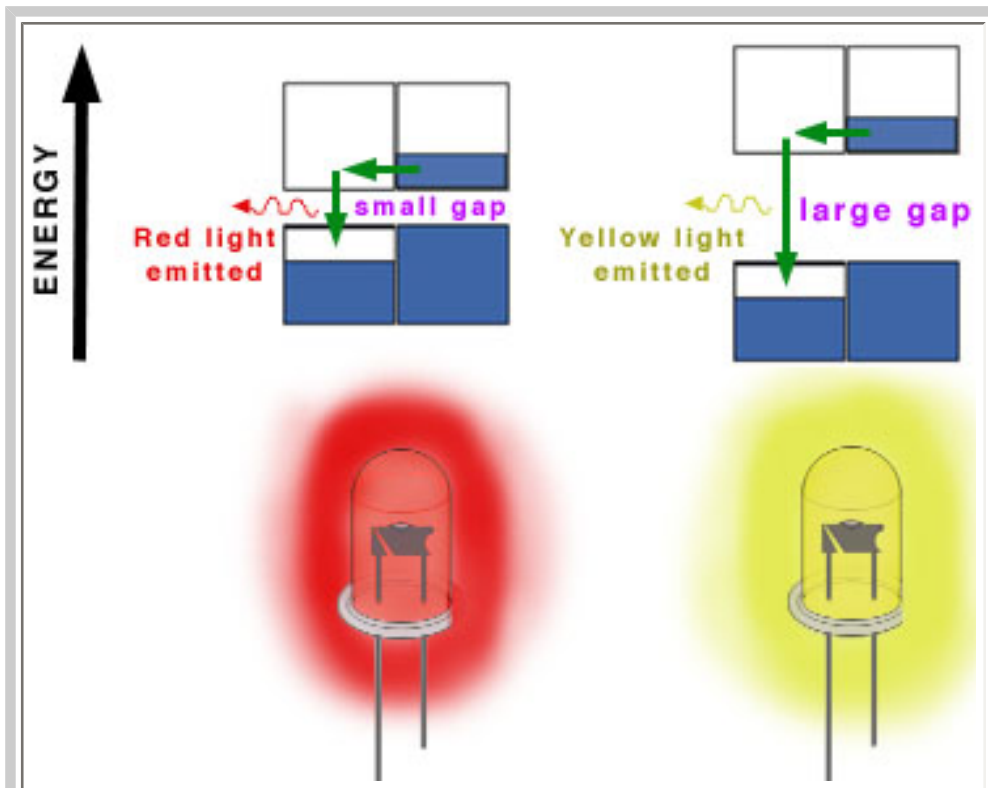


Figure 11

The color of light emitted by an LED depends on the size of the band gap in the doped semiconductors. For instance, LEDs that emit red light have a smaller band gap than LEDs that emit yellow light.

Questions on How LEDs Emit Light

- Explain, in terms of the movement of electrons, why an LED cannot be made from the junction of pure silicon (a non-doped semiconductor) and silicon doped with phosphorus (an *n*-type semiconductor).
- What element could the pure silicone in the question above be doped with, in order to produce an LED? Explain your answer.

Summary and a Look to the Future

In this tutorial, you learned that LEDs contain *p*-type and *n*-type semiconductors that are side-by-side. Semiconductors conduct electricity because of small band gaps between the

valence and conduction bands, which allow electrons to move throughout the material with a moderate input of energy. The LED emits light when the electrons fall from the conduction band to the valence band. The color of the light emitted depends on the size of the band gap.

Today's LEDs use inorganic material in the semiconductor. In 1990, the next generation of light-emitting material, the light-emitting polymer (LEP), was discovered. LEPs are organic (carbon-based) semiconducting materials. LEPs are based on the same chemical concepts taught in this tutorial. But LEP's could be used in more diverse applications than LEDs because polymers are flexible and can be shaped to different forms. At this time, however, technology based on LEPs is still in the experimental stages.

Additional Links:

- For a brief introduction about LEDs and a wonderful collection of images showing new applications for LEDs, see the tutorial from University of Wisconsin, "[LEDs - Light Emitting Diodes](#)"
 - The "[Lighting Futures](#)" site from Rensselaer Polytechnic Institute provides a wealth of information about LEDs, their applications, and new developments in LED technology.
 - For more information on [bonding and band theory](#), this tutorial provides explanations at several different levels of understanding.
 - Another interesting [research application for LEDs](#) is described on this page, by NASA.
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