# Light Emitting Diodes (LEDs)

Energy Characteristics of Electrons

The properties of metals are often explained using a model that these materials comprise a "negative sea of electrons surrounding positive islands of charge." While this is a very useful metaphor to describe electrical and thermal conductivity, it falls short in describing other properties of these and related solids. To develop a more versatile model, the energy characteristics of electrons need to be considered. Individual atoms are described as having nuclei that are surrounded by electrons that occupy regions in space, called orbitals, with characteristic probabilities and associated discrete energy levels. (Figure 1) Electrons fill the lowest energy levels first. A specific "quantum" of energy must be supplied to the electron in order for it to move to a higher energy level. Any one energy level (orbital) can have a maximum of two electrons in it whose spins must be paired. If two electrons are in the same orbital, they must "spin" in opposite directions so that each has a unique set of quantum numbers.
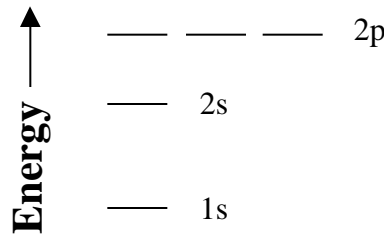
Figure 1. Energy diagram showing orbital energies.

Energy Bands

In the solid phase atoms are close together so their valence electrons have the ability to interact with one another. The core electrons have negligible interactions between atoms because they are closely associated with their nuclei. Discrete energy levels that are delocalized over the entire solid arise from the overlapping atomic orbitals. This collection of orbitals is tightly spaced in energy and comprises what is referred to as an *energy band*. Each band contains as many discrete levels as there are atoms in the crystal. Each orbital within the band can hold two spin paired electrons, just as was the case for isolated atoms. The figure below shows the energy bands of sodium. It illustrates that the highest occupied band of the alkali metals (the *3s* band in this case) is half-filled. Although magnesium, an alkaline earth element, has its valence *3s* bands filled and its valence *3p* band empty, there is an overlapping of the two bands, because the lowest levels of the *3p* band are lower in energy than the upper levels of the *3s* band. Therefore, some electrons overflow into the upper band.
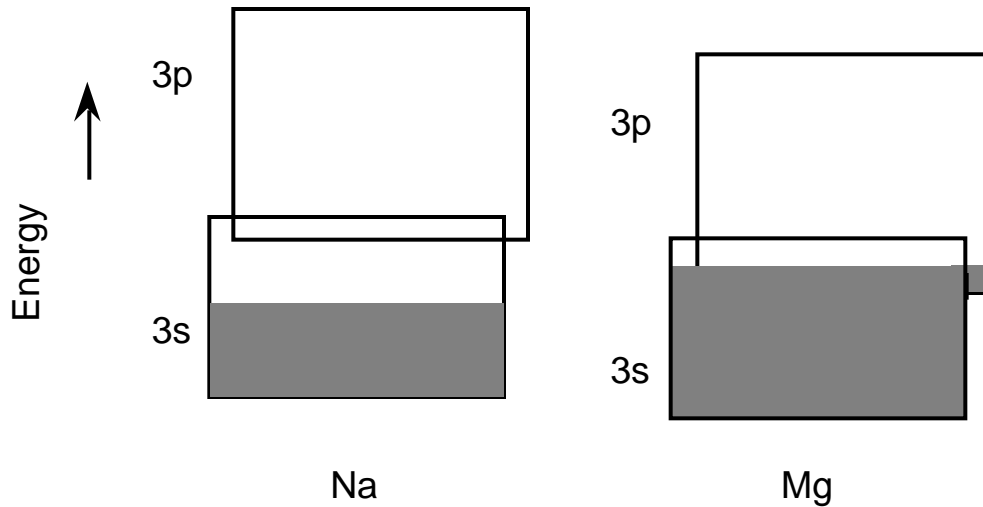
Figure 2. Energy bands of two elements.

In a band picture, band gap energy can be thought of as the energy needed to ionize (free) electrons from bands, enabling them to be mobile charge carriers. In descending the periodic table from carbon (diamond structure) to tin, the bonds become weaker, leading to a larger concentration of mobile carriers.

Conductivity and Energy Gaps

Band theory provides a framework for understanding electrical conductivity. The presence of charged particles and the ability for them to undergo net motion in a particular direction are the two conditions necessary for electrical conductivity. Valence electrons in solids are charged particles, and they move through the partially filled energy bands. Only electrons near the top of filled orbitals of partially filled bands contribute to conductivity. Metals are characterized by the presence of a partially filled band. In many other materials there are two bands to consider: a lower energy band that is filled with electrons, the valence band, and the next higher energy band that is unfilled, the conduction band. The energetic separation between these two bands is called the band gap energy. When the band gap energy is greater than about 3 eV, very few electrons can be thermally excited from the valence band into the conduction band at room temperature, and the material is an insulator. For band gap energies less than about 3 eV, some electrons can be thermally excited across the band gap, and the material is a semiconductor. A metal can be thought of as having a band gap of essentially zero.
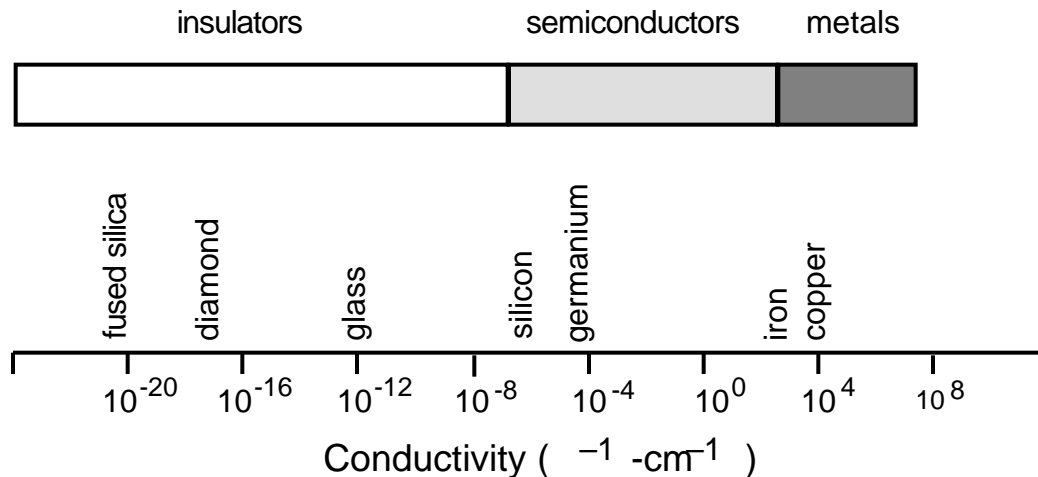
Figure 3. The entire range of conductivities of solids spans roughly 30 orders of magnitude. (From *A Materials Science Companion*, figure 7.7)

Most of the Group 14 elements have the diamond structure. In descending this group, carbon (diamond form) is an electrical insulator with a large band gap energy, silicon and germanium have smaller band gaps and are semiconductors, and tin, which has almost no band gap, is metallic. The difference can be explained by noting that as the atoms become larger and bond distances increase, orbital overlaps are reduced and the resulting energy gaps are smaller.
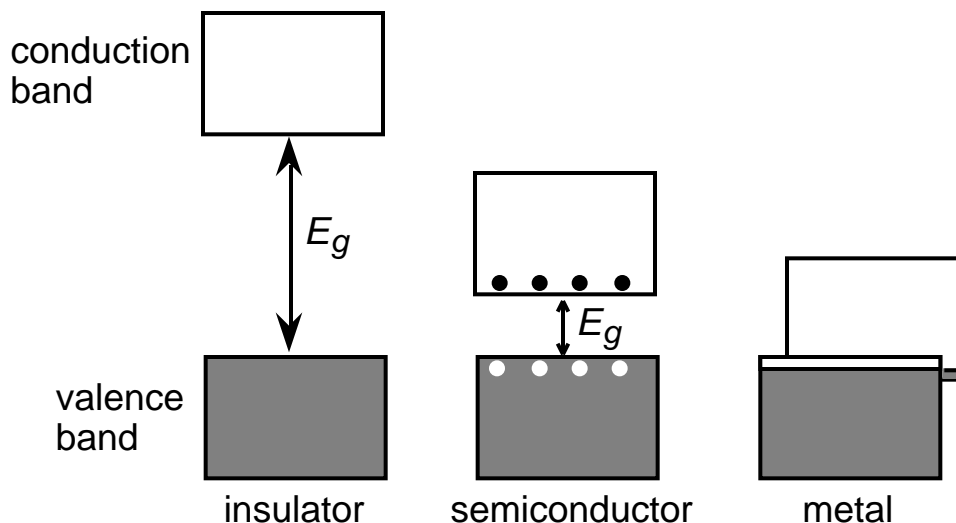
Figure 4. A general representation comparing the energy bands and gaps for insulators, semiconductors and metals. The conduction band and valence band of a metal actually overlap in energy resulting in a band gap energy of essentially zero. (From *A Material Science Companion*, figure 7.14)

The Zinc Blende Structure and Solid Solutions

  Elements having the zinc blende structure contain the same number of valence electrons and have AZ stoichiometry (1:1 ratio of elements). When all of the atoms are the same element, this is the diamond crystal structure. Solids such as Ge, GaAs, ZnSe, and CuBr are isoelectronic, which means they have the same number of valence electrons. Solids that contain atoms of comparable sizes and form the zinc blende structure can be combined in various ways to form solid solutions. Solid solutions are homogeneous solids in which one type of atom (or ion) has substituted for a similar atom (or ion) in a structure. These solid solutions are similar to some alloys in that different elements occupy specific sites in each others' crystalline structures. Having almost countless numbers of stoichiometries, it is possible to adjust or "tune" the band gap energies which depend on chemical composition. For example GaAs and GaP are only one of many pairs of semiconductors that may be combined to yield solid solutions, symbolized by the formula, GaP_xAs_{1-x} ($0 < x < 1$). The graph below clearly shows the increase in band gap energy from GaAs to GaP. This increase is primarily the result of the periodic trend in atomic sizes, since electronegativities of both As and P are about 2.0 and the electronegativity difference is constant. The smaller size of the P atoms allows the length of the unit cell edge to decrease, which enhances orbital overlap and increases the band gap energy.

F
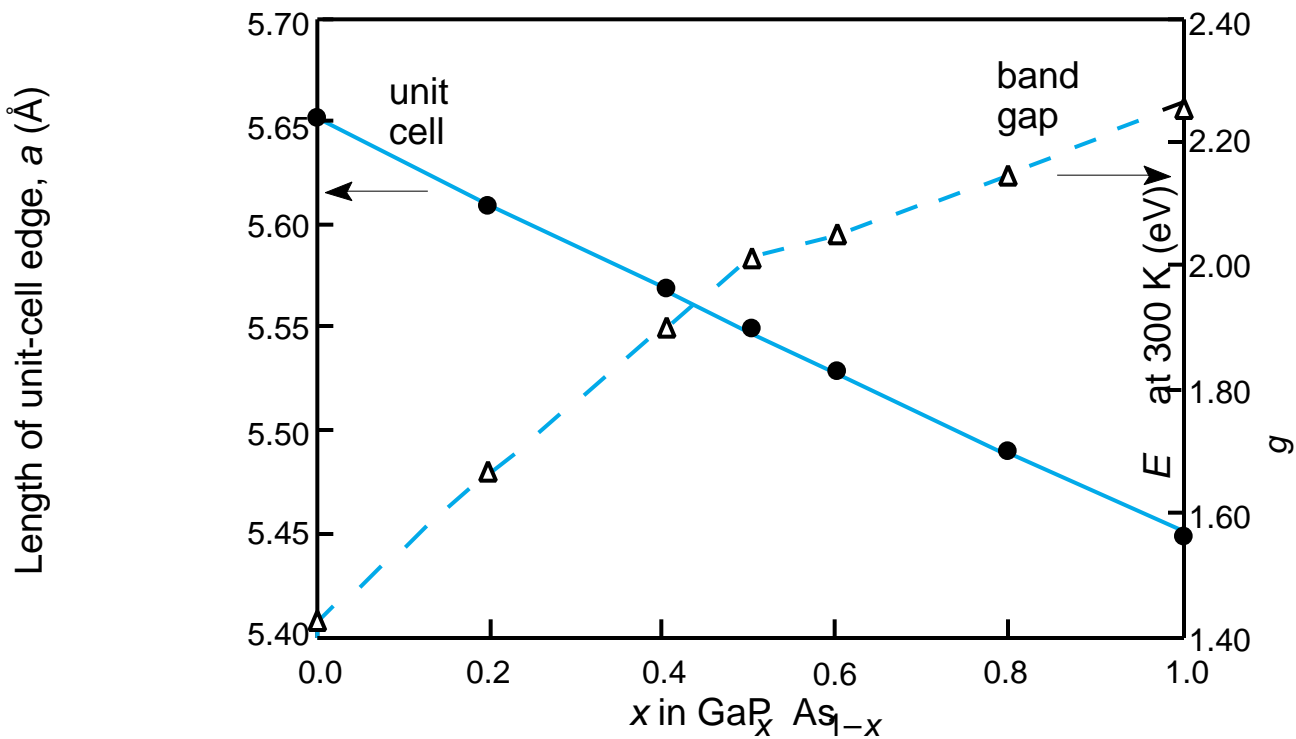
Figure 5. Trends in the cubic unit-cell parameter, a (Å), (filled circles), and the band gap at 300 K (open triangles) as a function of composition, x, for the solid solution series GaP_xAs_{1-x}. The kink in the band gap plot at x = 0.45 corresponds to a

change from a direct band gap to an indirect band gap. (From *A Materials Science Companion*, figure 7.19)
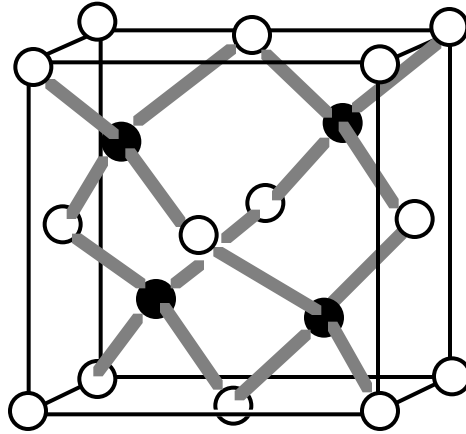
Figure 6. Drawing of a unit cell where all of the atoms are bonded to four other atoms. When all of the atoms are the same element, this is the diamond crystal structure. When the lighter colored spheres are different elements than the darker colored spheres, this structure has AZ stoichiometry and is called zinc blende. (From *A Materials Science Companion*, p. 407, figure 1)

		13	14	15	16	17
		B	C	N	O	F
		Al	Si	P	S	Cl
11	12					
Cu	Zn	Ga	Ge	As	Se	Br
Ag	Cd	In	Sn	Sb	Te	I
Au	Hg	Tl	Pb	Bi	Po	At

Figure 7: A portion of the periodic table emphasizing the formation of AZ solids that are isoelectric with Group 14 solids. Isoelectronic pairs are indicated with similar shading; for example Ge, GaAs, ZnSe, and CuBr. (**From** *A Materials Science Companion*, **p. 407, figure 2)**

Electrons and Holes

Conductivity in a semiconductor such as silicon can be described using the localized bonding picture. Each silicon atom is bonded to four other silicon atoms in a tetrahedral geometry. Since these bonds are relatively strong, the electrons are held tightly and are not mobile. However, a few electrons can be excited out of the bonds by either absorption of thermal energy or light of at least the band gap energy. As a result, electrical conductivities near room temperature can be appreciable.
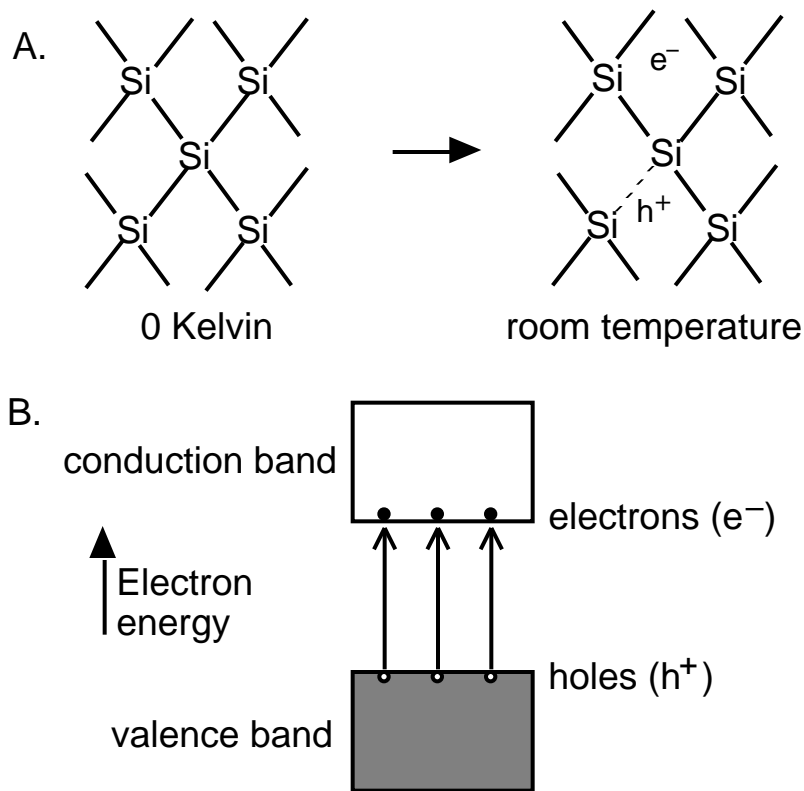

Figure 8. **A**: A localized bonding picture of a semiconductor. In the absence of heat or light, the valence electrons are localized in two-electron Si–Si bonds. However, absorption of heat or light energy produces some mobile electrons (e⁻) and an equivalent number of mobile holes (h⁺). The one-electron bond resulting from creation of the electron–hole pair is indicated with a dashed line. **B**: The band structure of a semiconductor using a delocalized bonding picture. Electrons (filled circles) may be excited from the valence band by absorption of light or thermal energy. Holes (open circles) are left behind in the valence band. (From *A Materials Science Companion*, figure 8.1)

One-electron bonds are created from these mobile electrons, and the missing electrons are often referred to as "holes." These missing electrons are treated as mobile individual particles and can be represented by h^+. The holes in the localized bonding picture roam throughout the solid, as electrons from adjacent two-electron bonds move to fill the holes. Consequently, the one-electron bonds become two-electron bonds but create new one-electron bonds. This process conserves the number of holes and effectively moves the holes throughout the crystal.
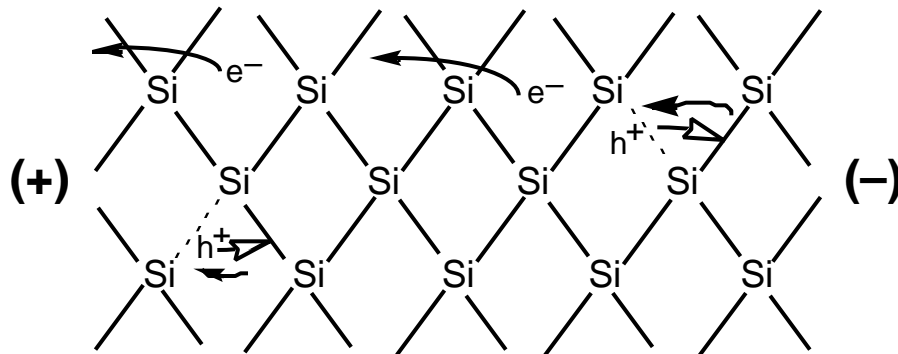

Figure 9. If a voltage is applied to a crystal of semiconducting material, the electrons migrate toward the positive terminal and the holes migrate toward the negative terminal. Two kinds of electron motion are illustrated. Excited electrons (e^-) move through the crystal toward the positive terminal. In addition, an electron in a bonding pair can jump into a one-electron bond (hole). This results in net motion of the electrons (dark arrows) and holes (open arrows) in opposite directions. This process of holes and electrons moving throughout a solid can be illustrated through a student demonstration. The picture below presents such a demonstration. (From *A Materials Science Companion*, figure 8.2)
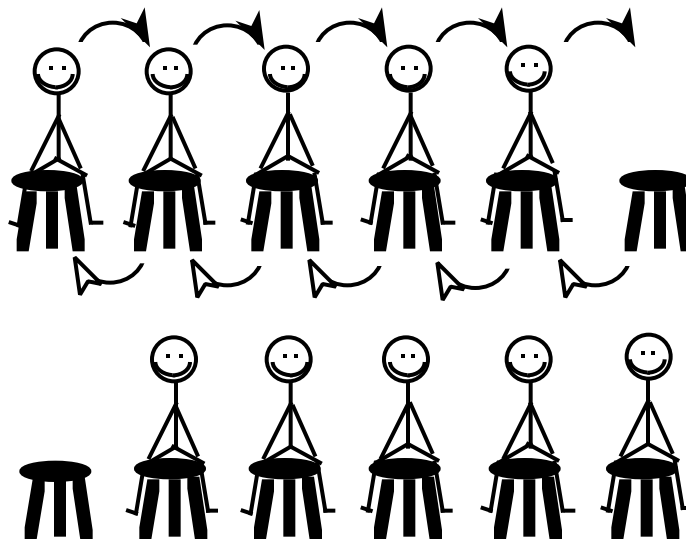
Figure 10. Hole mobility can be modeled by students. Five students are electrons and one empty chair is a hole. Having each student move one chair to the right (dark arrows) produces a result that is equivalent to the empty chair moving to the left (open-tipped arrows). (From *A Materials Science Companion*, figure 8.3)

Doping

It is possible to replace the atoms in a semiconductor with other atoms having more or fewer valence electrons, which will lead to an excess of mobile electrons or holes, respectively. This process is called doping. For example, replacement of silicon atoms with phosphorus atoms increases the mobile electron concentration and creates what is known as an n-type semiconductor (more mobile electrons than holes). Conversely, substitution of silicon atoms with aluminum atoms increases the mobile hole concentration and creates a p-type semiconductor (more mobile holes than electrons). Even substitution at parts per million level can cause million-fold enhancements in conductivity. This sensitivity is the reason for the use of clean rooms in the semiconductor industry and the kinds of clean room attire worn by industry personnel, as parts per million of contaminants can adversely affect electrical properties.
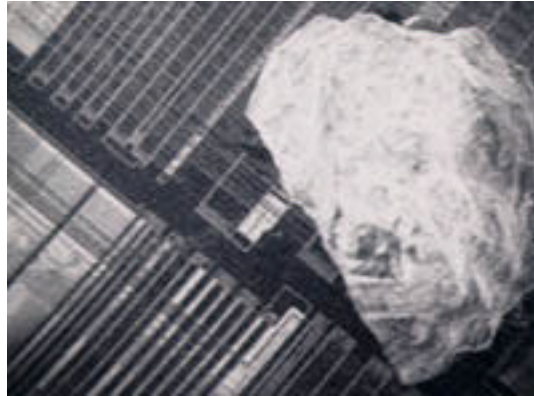
Figure 11. This enlarged image of a grain of salt on a piece of a microprocessor illustrates the small size and complexities of a microprocessor and the importance of clean rooms in manufacturing them.

A.   B.

Figure 12. **A**: If you´ve never done it before, putting on a bunny suit can take 30 to 40 minutes. The Intel pros can do it in five minutes. **B**: At the Intel Museum you can see what the Bunnypeople™ look like.

Light Emitting Diodes

There are two forms of semiconductors, n-type and p-type. An n-type semiconductor is one in which atoms with more valence electrons have been substituted into the structure of the original semiconductor. For example, a Group 15 atom could be substituted into the silicon structure. A p-type semiconductor is one in which atoms with fewer valence electrons (more holes) have been substituted into the structure of the original semiconductor. For example, a Group 13 atom could be substituted into the germanium structure. Now, if a low resistance metallic contact is made between an n-type and p-type material, the interface zone between them is referred to as a p-n junction. If a voltage is applied across this junction such that the n-type side is negative relative to that applied to the p-type side, the voltage is referred to as forward bias. Under forward bias the energy barrier for electrons and holes to flow through the junction is decreased, and negative electrons move from the n-type side to the p-type side, while positive holes are forced to move in the opposite direction.

A light emitting diode (LED) is a semiconductor p-n junction that is optimized to release light of approximately the band gap energy under forward bias, when electrons fall from the conduction band to the valence band. The electrons and holes migrate toward the junction where they recombine and release light whose energy corresponds to the band gap energy.

Uses and Capabilities of LEDS

LEDs are currently being used in various ways. One reason to use LEDs is that they last longer, and they are brighter, and are more efficient than incandescent lights. New flashlights made with LEDs are making their way into the marketplace. LEDs are

also extremely tough. This characteristic is a result of having no glass to shatter and no filament to break. Therefore, the new LED lights are shockproof and more robust than incandescent lights. Extremely efficient, the LED lamps use as little as ten percent of the electricity that an incandescent light uses. Consequently, if a light is battery-operated, an LED design requires far less battery power. Incandescent light bulbs burn out after about 25-100 hours of use, while LEDs have life spans of 100,000 hours, which is over 11 years of continuous use.

   The trait of efficiency goes hand in hand with being environmentally friendly. As a result of the LED's efficiency, LEDs do not waste as much electricity nor require large supplies of batteries. They can also be solar-powered.

    In addition to these reasons, LEDs are safer and more reliable. LEDs are excellent for use near explosive gases and liquids, since they can withstand large shocks and vibrations and operate at a low temperature. Due to their low failure rate, they reduce liability, especially in areas where a failed light could cause an accident. Many lights are used to warn people or to permit people to work at night under safe conditions. Light failure can result in substantial cost if it leads to an accident or lost labor.

   In the automotive industry LEDs are becoming prevalent. The new lights improve automobile safety and reliability while cutting design and assembly costs. The LEDs eliminate the need for deep cavities in the car body that were required for incandescent lights. This in turn eliminates the expensive sheet-metal tooling and assembly costs associated with body cutouts required for other types of lighting. As a result, more trunk space is available and designers have flexibility in altering the car's appearance. LEDs consume less power than incandescent bulbs, which in turn frees up more electrical energy for other parts of the vehicle. This also helps with fuel economy. LEDs in vehicles are safer. Because LEDs do not require the heating of a filament to produce light, they illuminate faster than incandescent lighting, which gives drivers more time to react to other cars in front of them on the road.   This cuts down on the number of accidents that occur. Therefore, LEDs with characteristics such as low power consumption, long lifetimes, brightness, and safety are increasingly being used everywhere. Here are some other examples of where they are being utilized.

- Bi-color LEDs used in programmable message boards
- Roadside vehicle speed display
- Brake lights on automobiles
- City buses, which have brake and tail lights as well as turn signals
- Some traffic signals
- Electrik Art-prints (http://www.cybershop2020.com/electrik.htm)
- New railroad crossing flashers
- Exit signs
- Parking information signs
- Construction sign traffic arrows