LEDs: New Lamps for Old and a Paradigm for Ongoing Curriculum Modernization

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A Paradigm for Updating the Curriculum

There is increasing recognition that chemistry curricula can effectively draw on modern research and technology to provide compelling story lines for communicating core principles. Modules, for example, are now available for introductory chemistry courses that convey fundamental concepts through such themes as air-bag design, preservation of the ozone layer, olestra fat-substitute chemistry, and construction of semiconductor light-emitting diodes (LEDs) (1). These nontraditional forms of content permit instructors to connect chemistry to emerging, often interdisciplinary, fields such as environmental science, materials science, and biotechnology (2).

Cutting-edge research and technological advances are frequently identified in research- and applications-driven white papers, “road maps”, and future-directions articles (3, 4). We believe that these summaries of research and technical opportunities are an underutilized rich source of up-to-date instructional materials. In this paper we present a paradigm for use of such materials. A recent white paper identifies LEDs as potential replacements for a significant fraction of vehicle, traffic, display, home, and workplace lighting, with substantial safety and energy- and environment-conserving benefits (5). One of our objectives is to summarize key results from this study that will engage student interest.

Another objective is to identify examples from this technology that instructors can use to illustrate core chemistry topics. Such correlations have been published for semiconducting materials using a topic matrix (6). These correlations, which are updated and expanded in this article, embrace a variety of periodic trends in a family of essentially isostructural solids. The stoichiometry of these solids can be routinely tuned to include three and even four elements using the periodic table as a design tool. From a bonding standpoint, these solids illustrate a variety of trends in periodic properties, including electronegativity, atomic radii, bond polarity, and isostructural principles. From a spectroscopic perspective, colors of emitted light can be correlated with physical and electronic structure.

Semiconductors provide an acid–base and concentration cell system that complements traditional presentations of aqueous systems. For more advanced treatments, the quantum mechanics of spatially confined particles can be presented with this family of solids, demonstrating the remarkable control that exists in the growth of semiconducting materials.

Background to the LED White Paper

Lighting is such a routine part of our lives that it is easy to overlook the profound changes in lighting technologies being brought about by LEDs. As is reported in the white paper, arrays of these small, bright light sources are being introduced into a variety of traditional lighting venues, yielding substantial energy and safety benefits (5). Worldwide, lighting applications consume about 20% of all electricity generated. The luminous efficiency of recently developed high-efficiency LEDs exceeds that of incandescent bulbs (Fig. 1). Estimates predict that the widespread replacement of incandescent and fluorescent lighting with LED-based lighting could decrease this consumption by 50%, a global savings of more than $100 billion/year. As a consequence of this lower demand for electricity, the carbon emissions created during the generation of electricity could be significantly reduced.

Traditional incandescent light bulbs are blackbody emitters. A filament, typically tungsten, is resistively heated to a sufficiently high temperature that a portion of the emitted electromagnetic radiation is in the visible part of the spectrum (Fig. 2). Most of the energy is wasted as heat. At high temperatures, the filament sublimes, leading to a thinner wire with yet higher electrical resistance and enhanced susceptibility to sublimation. As this process naturally accelerates, it leads to failure of the filament. A standard 100-W incandescent bulb has an average lifetime of 1,000 hours, or about 84 days if it is used 12 h per day (5).

In contrast, electrons supplied to an LED enter excited-state energy levels. As these electrons relax to the ground state, energy corresponding to the difference in energy levels is...
emitted in a narrow band of wavelengths. The periodic properties that control the energy levels in the solid—atomic size and electronegativity—also control the wavelength of light emitted (2, 6–9). Current LEDs have an expected lifetime of 100,000 h (5). It is estimated that even when driven at their maximum rated current, LEDs will be usable for on the order of 10 to 100 years, (out)lasting the lifetime of most products into which they will be incorporated. Disposal should pose little environmental threat, as the chips (the block comprising layers of semiconducting material that are subjected to a voltage to yield current and light), which currently contain principally Al, Ga, In, N, and P, are encased in a robust plastic housing.

The typical semiconductor LED chip (or die) has dimensions of a few tenths of a millimeter. It is encased in a polymer lens that helps focus the light and holds the electrical connections in place. One electrical connection is typically made by attaching the die directly to a lead that also performs the functions of heat dissipation and reflecting light into the desired radiation pattern. The other connection is made by a gold wire connection from the die to a second lead. The leads provide the principal means of heat dissipation for the electrical energy that does not become light. The size of a semiconductor LED is limited by the quantity of heat produced. Changing the LED packaging to include a larger heat sink has recently permitted construction of LEDs that are more than an order of magnitude brighter than those previously used in many applications.

The principal cause of LED failure is damage of the polymer housing, through either passage of too large a heat-generating current, exposure to ambient UV light, or damage to the LED die resulting from mechanical stress within the housing.

### Applications of LEDs

In comparison to incandescent bulbs, LEDs are smaller, longer lived, more energy efficient, more robust, less heat generating, and more directional, and they have faster switching times. The relative monochromaticity of LEDs compared to energy-inefficient filtered incandescent bulbs makes them advantageous in a variety of applications involving colored lights (5). Part of the apparent vividness of the color associated with an LED is due to this monochromaticity or high color saturation. In the remainder of this paper, we discuss the wide

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**Figure 1.** Plot of log (luminous efficiency) versus year for LEDs, showing that many LEDs are now more efficient than incandescent lamps; efficiencies are expressed in lumens of light output per watt of electrical input. LED compositions and their corresponding emission color are indicated in the graph; three- and four-element formulas like AlGaAs and AlGaN represent solid solution compositions, wherein the emission band maximum can be tuned with composition, as described in the text and in refs 6–9 and 23. Elements following the colons in these chemical formulas represent dopants employed to improve the LED efficiency, and compositions following a slash (/) are the substrate. Adapted from ref 25. We are grateful to M.G. Craford of Lumileds for this figure.

**Figure 2.** Comparison of spectral outputs of red traffic lights. The narrow peak with \( \lambda_{\text{max}} \) at ~640 nm is the spectrum of the red LED traffic light. The broader spectrum is the output of an unfiltered incandescent bulb used in a traditional traffic light. When this bulb is covered with a red plastic lens, wavelengths exceeding ~600 nm (vertical line in the figure) are transmitted, accounting for the red color.
range of LED applications related to these characteristics and summarize some of the chemical and physical properties underpinning the replacement of incandescent lights with LEDs.

**Vehicle Lighting**

LEDs are increasingly being used for exterior lights on automobiles, trucks, and buses. LED brake lights and rear turn signals are installed as original equipment and retrofitted onto buses and trucks as incandescent bulb assemblies burn out or are damaged (Fig. 3) ([10](#)). It is expected that as the cost of LEDs decreases, they will replace nearly all of the exterior and interior lighting of vehicles.

Four major reasons for the switch to LEDs are energy savings, durability, design flexibility, and safety. The use of LEDs in motor vehicles reduces the amount of electrical power required by the vehicle. This allows more power for other applications or the use of a smaller generator or alternator.1

A drawback of incandescent bulbs is their susceptibility to failure from the mechanical shocks and vibrations associated with moving motor vehicles. LED assemblies should last the life of the vehicle. The ability to permanently solder LEDs to printed circuit boards also reduces manufacturing costs.2

The fact that LEDs are small allows considerable design flexibility. For example, tail light assemblies can be placed in such spatially restricted locations as the roof of vans and trucks and the spoilers on the backs of automobiles (Fig. 3).3 Their wide range of colors allows LEDs to be used in instrument displays for information about the operation of the vehicle. For example, blue LEDs are used to indicate that the vehicle’s bright headlights are in operation, green LEDs identify turn signal usage, red LEDs alert the driver to conditions requiring immediate attention, and orange LEDs provide less urgent warnings related to low fuel and servicing needs. The reduced size and heat generation of LEDs compared to incandescent bulbs allows greater information density on the instrument console ([10](#)). LEDs are also more compatible with the microprocessor logic that supplies information to the instrument console ([10](#)).

Traffic Control Signals

For reasons of energy savings and safety, LED arrays are finding increasing use in traffic lights, vehicle speed indicators, pedestrian crossings, construction signals, and railroad crossing flashers (Fig. 4). Although red LED traffic signals are most common, amber and green LEDs also now meet the color standards of the Institute for Transportation Engineers, and energy savings can be realized in both new LED traffic-control signals and retrofitted units. A single-color incandescent traffic light consumes 150 W, whereas a brighter LED traffic light consumes about 20 W of power ([13](#)). Relative to red LED traffic signals, the slower adoption of amber and green LED traffic signals reflects their longer payback times, which are due to reduced illumination periods (amber) and higher manufacturing costs (green) ([5, 14](#)). LED traffic arrows use only 8 W compared to the 150 W required for turn arrows constructed from an incandescent bulb with a mask. The savings arise in part because only enough LEDs to form the arrow are needed ([10](#)). Similarly, pedestrian Walk/Don’t Walk lights operate at 8–12 W,
compared to the normal 70 W used by incandescent bulbs \((15)\). When scaled over the number of traffic control signals in the world, use of LEDs offers significant savings in global energy usage.\(^4\)

The redundancy of the LED array is a particularly important safety feature: failure of a single element is not catastrophic, since there are typically more than 100 LEDs on a single traffic light, depending on size. In fact, many of the LEDs can fail and the light will still operate.\(^3\) New designs with only 12–18 high-power LEDs still provide significant redundancy \((16)\).

LEDs also reduce maintenance costs. In addition to the cost of emergency replacement of failed incandescent bulbs, routine maintenance of traffic signals calls for the replacement of all red and green incandescent bulbs annually and of amber traffic signals every two years \((10)\).\(^6\) LED traffic lights are expected to have significantly longer lifetimes.

**Message Boards and Large Array Displays**

LEDs are providing a new generation of display technologies because of energy savings, color mixing, and brightness. Illustrating energy savings are lighted interior EXIT signs (Fig. 4). A typical 100-LED sign will consume less than \(\frac{1}{3}\) the energy of conventional compact fluorescent lamps. Newer signs with as few as six high-power LEDs provide the same energy savings. This low power consumption also means that the LED-based sign stays lit longer on battery backup power \((5)\). Solar-powered LED displays are currently used on roadway construction sites. The solar panels generate sufficient power to run the display during daylight hours and to charge the batteries for use during the night. In contrast, portable displays with low-efficiency incandescent bulbs require use of a noisy and polluting gasoline-powered generator.

Television monitors and computer screens use combinations of red, green, and blue to produce millions of different colors. The development of the blue and green LED chips using GaInN technology, in conjunction with red chips based on AlGaInP technology \(\text{(see below and Fig. 1)}\), has permitted creation of red, green, and blue pixels that can be used for large-area, full-color video displays \((9, 17)\). Virtually all portable devices, from key-chain flashlights to cell phones, will benefit from the excellent reliability and low power consumption of LEDs.

**Novelty Applications**

LEDs are appearing in products ranging from model railroad lights to yo-yos to children’s athletic shoes to writing pens to ornaments. Model railroads have experimented with LEDs for years in miniature signals, and white LEDs are beginning to replace tiny incandescent bulbs as headlights in model railroad locomotives \((22)\). Virtually all portable devices, from key-chain flashlights to cell phones, will benefit from the excellent reliability and low power consumption of LEDs.

**The Chemistry of LEDs**

Detailed descriptions of the materials used in LEDs and the devices’ construction have appeared \((2, 6–9, 23)\). Recent developments and the key concepts underpinning these devices are summarized below.

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**Figure 5.** Giant outdoor LED displays like this Sony JumboTron in the center of the Liberty Bowl Stadium scoreboard in Memphis, TN, are being used to show live video and instant replays.

**Figure 6.** LEDs of any color can be arranged in a cluster that will fit into a standard incandescent bulb socket, such as the red cluster shown here.
### Analogies to Acid–Base Chemistry and Concentration Cells

The crystalline semiconductors used in the construction of LEDs, like all semiconductors, are characterized by a band gap energy. In a simple bonding picture, the band gap energy can be regarded as the energy required to ionize an electron from a bond in the solid, permitting it to become mobile and contribute to electrical conductivity. The remaining one-electron bond is also mobile and can be thought of as a positively charged particle called a hole. (An electron from a nearby two-electron bond can “fill” the one-electron bond, creating a new one-electron bond in the process and, in effect, moving the hole.) When mobile electrons occasionally restore a two-electron bond by recombinating with a hole, they liberate energy as heat and/ or light. The latter process is called radiative recombination and the energy released will be in the form of photons possessing roughly the band gap energy and occurring at a corresponding wavelength given by the Planck relationship, \( E = h \nu \) (6).

This creation and recombinating of electron–hole pairs in a 1:1 ratio is reminiscent of autoionization in water and is governed by a similar temperature-dependent equilibrium constant. In water, the product of the proton and hydroxide concentrations is typically expressed as \( K_w = [H^+] \times [OH^-] \). The analogous equilibrium in semiconductors is described in terms of the concentration of mobile electrons \( n \) and mobile holes (missing electrons) \( p \), with \( K = n \times p \). Just as acids and bases can be used in water to increase the proton or hydroxide concentration, respectively, at the expense of the other, impurities called dopants can be deliberately added to semiconductors to adjust the relative values of \( n \) and \( p \). In GaAs, for example, substitution of Zn for Ga or of Se for As can increase \( p \) or \( n \), respectively, because the substituting atom has fewer or more valence electrons than the atom it replaces. When the concentration of electrons exceeds that of holes through doping, the material is described as n-type; and when the concentration of holes exceeds that of electrons, the material is p-type (6).

By growing semiconductors in which the p-type layer is in contact with the n-type layer, a p–n junction is created that is characterized by a built-in voltage. This voltage results from the difference in electrochemical potentials of the n- and p-type materials and is analogous to the voltage that can be obtained from an aqueous concentration cell having different proton concentrations (pH) in the two electrolytes. When a voltage is applied to a p–n junction in one direction (forward bias) (Fig. 7), mobile electrons on the n-type side can easily cross to the p-type side where they have a high probability for recombinating with the large pool of holes in this region, leading to efficient emission of band-gap-energy light. Similarly, mobile holes in the p-type region can cross to the n-type side and have a high likelihood for radiatively recombinating with electrons, the majority charge carriers in this region. With a voltage applied in the opposite direction (reverse bias), there is a substantial barrier for electrons or holes to cross the interface, and little current flows. This pronounced directionality of current flow with applied voltage is the essence of diode behavior and is a property of LEDs (2, 6–9).

### The LED Palette and Periodic Properties

The color of light emitted by an LED can be tuned by varying the semiconductor composition guided by periodic trends that involve atomic radii and electronegativity. Descending a group in the periodic table leads to larger internuclear distances (6, 10). As the internuclear distance increases, the bonding electrons are held less strongly, and their more facile ionization corresponds to a smaller band gap energy. For example, the band gap energies of the binary semiconductors GaP, GaAs, and GaSb are 2.3, 1.4, and 0.7 eV, respectively (24). The internuclear separations in AlAs and GaAs are almost identical, but the larger band gap energy of AlAs, 2.1 eV, reflects the greater polarity and strength of the Al–As bond compared to the Ga–As bond (6).

Even greater tunability in band gap energies is achieved through the use of solid solutions (alloy semiconductors). Two semiconductors with the same crystal structure can often form solid solutions in which one atom substitutes for the other in any proportion if the substituting atoms are chemically similar. For example, the band gap energies of the ternary solids Al\(_x\)Ga\(_{1-x}\)As (0 ≤ \( x \) ≤ 1) can be continuously tuned from 1.4 eV to 2.1 eV as \( x \) varies from 0 to 1. With quaternary solids additional design flexibility is available, because unit cell size can be varied while retaining the band gap energy. Alternatively, the band gap energy can be varied while maintaining the size of the unit cell (lattice constant) (6). The latter is extremely important in growing high-quality devices comprising layers of semiconductors, as it permits materials with different band gap energies to be grown atop one another so that the atoms of the growing layer are in alignment with the substrate, a process called epitaxial growth. This technique may minimize the number of defects at the interface of the...
junction between the materials that might otherwise degrade the performance of the LED (25).

**Preparation of LEDs**

The design and preparation of LEDs exemplifies exquisite control both of chemical composition and materials growth, resulting in devices with tailored electro-optical properties (26). Techniques such as organometallic vapor-phase epitaxy (OMVPE, also known as metalorganic chemical vapor deposition, or MOCVD) provide kinetically controlled growth of semiconductor layers, which can be used to localize and optimize radiative recombination of electrons and holes in the solid (27). As noted above, the chemical composition of the layers controls their band gap energy and thus the color of light associated with the emitted photons that result from radiative recombination (28).

The group 13–15 semiconductors (called III–V semiconductors by researchers in the field) comprising the layers of LED dies are produced through co-decomposition of group 13 and group 15 precursor gas molecules. For example, using highly purified gases like trimethyl gallium and arsine, a layer of semiconducting GaAs can be formed by the decomposition of the gases on a heated substrate, according to eq 1.

\[
(CH_3)_3Ga(g) + AsH_3(g) \rightarrow GaAs(s) + 3CH_4(g)
\]  

(1)

Such growth techniques permit chemical composition to be altered virtually in an atomically abrupt manner by changes in the concentration and composition of the gaseous precursors (Fig. 8a). A more general, unbalanced equation for tuning chemical composition is eq 2, where the value of \( n \) can be 0, 1, 2, or 3, reflecting the composition of species derived from the trialkyl precursors that are present under growth conditions:

\[
x(CH_3)_yAl(g) + y(CH_3)_zGa(g) + z(CH_3)_6In(g) + PH_3(g) \rightarrow \]

\[
Al_xGa_yIn_zP(s) + CH_4(g)
\]

(2)

The product subscripts indicate that these materials form a family of solid solutions, possessing, in this case, a common cubic zinc blende crystal structure but variable composition with \((x + y + z) = 1\) (6). Typically, chemical compositions that are nearly lattice-matched are used so that the atomic layers continue to grow epitaxially and defects are minimized.

The emergence of the LED as a versatile lighting source reflects the use of new atomic compositions that embrace the entire visible spectrum and yield brightness and efficiency that rival traditional incandescent lamps. A summary of these compositions that can be denoted as \((Al_{x}Ga_{1-x})_{0.5}In_{0.5}P\) (0 ≤ \( x \) ≤ 1) have been found to yield superior LED characteristics. Figure 9 presents a plot of band gap energy and associated emitted wavelength versus lattice constant for the AlGaInP family of solid solutions. The lower and higher edges of the shaded region correspond to the ternary compositions \(Ga_{x}In_{1-x}P\) and \(Al_{x}In_{1-x}P\), respectively. The interior shaded region comprises the quaternary \(Al_{x}Ga_{y}In_{z}P\) compositions. Note the vertical dashed line in the figure, which corresponds to \((Al_{0.3}Ga_{0.7})_{0.5}In_{0.5}P\) compositions. This line illustrates how band gap energy increases from ~1.9 eV to ~2.3 eV—from the red to the green part of the visible spectrum—with increasing Al content while maintaining a lattice constant of 5.65 Å.

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**Figure 8.** (a) Chemical composition can be controlled at the nanoscale. This scanning electron microscope (SEM) image shows various thicknesses of GaAs layers sandwiched between thicker (50-nm) \(Al_{0.3}Ga_{0.7}As\) layers, forming so-called quantum wells. (b) Emission from a set of quantum wells like those shown in (a), illustrating that emission energy increases as thickness, labeled on the spectrum, decreases.

**Figure 9.** Diagram of band gap energies and corresponding wavelengths as a function of atomic bond distances, as represented by the cubic unit cell lattice constant for AlGaInP compositions having the zinc blende structure. The three corners labeled with open circles correspond to pure binary phosphide phases. Solid edges represent ternary solid solutions derived from the corner compositions. The shaded interior represents quaternary solid solutions of AlGaInP; the compositions below the interior solid line are highly emissive and used to construct LEDs. Compositions lying on the vertical dashed line have the same unit cell size as GaAs and can be grown epitaxially on this substrate. Adapted from ref 26.
Within the past few years another significant breakthrough has been the development of robust, efficient GaInN compositions to access the blue and green parts of the visible spectrum. Interestingly, LEDs prepared from these materials operate effectively despite having very high defect densities (25).

Future breakthroughs in the use of LEDs will hinge on new materials and improvements in synthesizing semiconductors so as to achieve even better control of the nanoscale structure of the resulting devices. An emerging technology is the use of organic compounds for construction of LEDs. These organic LEDs (OLEDs) may offer substantial benefits in cost, size, weight, processability, and environmental impact that could make them competitive in a variety of lighting applications (29, 30).

Further advances in controlling nanostructures of traditional LED materials can also be expected. The “particle in a box” that is a mainstay of physical chemistry courses can be grown with thin semiconductor layers known as quantum wells (31, 32). Figure 8b shows the emission spectrum of a material similar to that described in Figure 8a. Emission occurs at higher energy when electrons are confined to thinner layers (i.e., a particle in a smaller “box”). The increasing sophistication with which we can create customized structures on the atomic scale suggests that industry goals of 45% efficiency for LEDs throughout the visible spectrum will soon be within our grasp.

Conclusion

As indicated by these many applications, LEDs are causing profound changes in lighting technology. The ability to mass-produce the semiconductor compositions comprising these small devices using modern materials growth methods, coupled with their desirable operating characteristics, are permitting arrays of LEDs to replace traditional lighting sources with considerable safety and economic benefits. These developments readily lend themselves to incorporation into the chemistry curriculum as examples of the application of chemical principles to cutting edge research and technology. Industry white papers and “road maps” and “future directions” articles often provide excellent summaries of such research breakthroughs and their potential economic and technological impact. They can thus be used as resource materials for updating the curriculum and connecting chemistry to other disciplines.


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Notes

1. The weight of the vehicle is reduced a small amount with LEDs because the lower power requirements allow thinner, lighter wiring to be used. This reduces the load on the motor and results in lower fuel consumption, an industry objective. The use of LED turn signals can extend by a factor of 2 to 3 the amount of time that the emergency flashers can operate on battery power. The low operating temperatures of LEDs permit them to be weather-sealed with inexpensive, low-melting plastics.

2. A major LED manufacturer estimates that as much as $80 million in warranty repair costs could be saved by using LEDs for the rear exterior signal lights on the 15 million cars and light trucks produced each year in North America (33).

3. One of the first applications of LEDs was in the center high-mound stop lamp (CHMSL), which became mandatory on U.S. vehicles in 1982. By 1999, 30–40% of new cars had LED CHMSLs. For some year 2000 models, the tail, brake, and turn signal lights are all LEDs (5, 34).

4. In the United States alone, 10 million red/yellow/green traffic lights consume about 400 MW (3.5 terawatt-hours annually) of electricity. At $0.07 per kilowatt-hour, the cost of operating U.S. traffic lights is $240 million annually. Replacing only the red signals and arrows would save about 250 MW, and the estimated payback period for the red LED signals is significantly less than one year (5). Conversion to LED traffic signals would save 70 MW (enough power for 70,000 homes) in California (15, 35). Since the lower power consumption would help avoid the expense of building additional power plants, many utility companies (e.g., Pacific Gas and Electric in California; Northern States Power in Minnesota, Wisconsin, North Dakota, South Dakota, and Michigan; GPU Energy in New Jersey) have offered rebates to cities that install LED traffic lights (36–38).

5. In a test by the state of Oregon, several shots from a 9-mm weapon were fired at a 12-inch traffic signal module from a distance of 25 feet. While 112 of the more than 600 LEDs failed, there was no effect on color and the module was considered viable from 50 to 75 feet (10).

6. This operation requires at least two persons with a bucket truck, costing about $250 per intersection.

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