LEDs Challenge the Incandescents

Materials that make light-emitting diodes brighter and less power-hungry open exciting new applications for semiconductor lamps

by M. George Craford

More than 20 billion visible light-emitting diode (LED) chips are produced each year. As a packaged lamp, each of these LEDs typically costs less than ten cents, and are used in a variety of display products generating yearly sales of about a billion dollars.

The emergence of high-brightness red AlGaAs emitters opened new markets to visible LEDs. The recent introduction of AlInGaP yellow and orange devices, with their order-of-magnitude improvement in luminous performance,* are expected to further increase the growth rate and offer a viable alternative to incandescent (filament-based) lamps. Green-emitting AlInGaP devices should also have an efficacy substantially better than that of existing technology.

The efficacy of commercial LEDs has increased by a factor of 20 over the past 20 years (Fig. 1). Commercial red-emitting GaAsP devices first became available from Monsanto and Hewlett Packard in the late 1960s, following the work of Holonyak in 1962 [1]. They were soon joined by the red-emitting gallium phosphide devices doped with zinc and oxygen (GaP-ZnO), which initially performed better.

* The luminous performance is the luminous (visible) flux output of a light source measured in lumens divided by the electrical power input to the device. Lumens are calculated by multiplying the radiant flux output of a device (in watts) by the human eye’s sensitivity as defined by the Commission Internationale de L’Eclairage, or CIE. The concept is akin to efficiency, i.e., the useful output in relation to the power input, but the term “efficiency” does not apply because the lumen is not a unit of power.
The performance of these early red LEDs was in the range of 0.1 lumens of output flux per watt of input electrical power, more than 100 times lower than a typical 60-to-100 watt incandescent lamp (which produces about 15 lumens/watt). As a result, LEDs were used primarily for indicators in indoor applications, where low light levels are adequate. Red LEDs made possible the introduction of electronics in watches and calculators in the early 1970s, but they were replaced with liquid crystals, which permitted longer battery life and better visibility in sunlight.

A technical breakthrough occurred in 1968 with the addition of nitrogen, an iso-electronic dopant that contributed efficient radiative recombination centers to GaP [2] and, in 1971, to GaAsP [3,4]. Iso-electronic dopants occur in the same column of the periodic chart as the host crystal; in this case, Column V, and do not add charge carriers.) Soon, GaAsP:N LEDs with performance in the range of 1 lumen per watt were available in red, orange, and yellow. GaP:N provided similar performance for green devices. These developments allowed visible LEDs to penetrate new application areas and grow in production volume despite the loss of watch and calculator applications.

The next major breakthrough in LED technology was the development of red-emitting AlGaAs devices in the early 1980s that produced from 2 to 10 lumens/watt, depending upon the structure used [5-6]. This advance enabled LEDs to compete with incandescent lamps for automotive taillights, outdoor moving-message panels, and other applications that require high flux output.

A typical incandescent automobile taillight emits roughly 15 lumens/watt of white light, but the red filter absorbs about 75 percent of the light, resulting in 3 to 4 lumens/watt of red light — substantially less than the best LEDs. Designers often choose LEDs for their other favorable characteristics, notably higher reliability and design flexibility. Using a row of LEDs in an automobile’s “spoiler” to replace the conventional rear-window brake light is one example of this flexibility.

AlGaAs LEDs are only available in the color red, which denotes stop or danger. This is ideal for the “third brake light,” but it makes AlGaAs unsuitable for many other applications.

In 1990, C. P. Kuo and his co-workers reported their development of a yellow AlInGaP LED with performance comparable to the best red AlGaAs devices, and about ten times better than the then-standard GaAsP:N yellow LEDs [7]. By varying the alloy composition, device designers can fabricate AlInGaP LEDs that provide high brightness from the red through the green spectral regions. These devices are allowing LEDs to enter applications that require either high output power or low current consumption.

Blue has been the missing color in bright LEDs. Blue LEDs have been available since the early 1970s, but their performance has been (and continues to be) low compared to the longer-wavelength devices. Although blue LED performance is still below 0.1 lumens/watt, SiC blue types of LEDs are grown with different techniques and have different characteristics (see Table). What the active layers of most LEDs have in common is that they are produced by epitaxial growth, i.e., the growth of thin single-crystal layers on single-crystal substrates. The technologies that together dominate about 90 percent of the market are:

- **GaAsP:N**, grown by vapor-phase epitaxy (VPE), in which gas is used to transport the relevant elements, and
- **GaP:N** and **GaP:ZnO**, grown by liquid-phase epitaxy (LPE), in which liquid gallium is the transport medium.

VPE and LPE are mature, cost-effective technologies that have been in use for more than 25 years. Metalorganic chemical vapor-phase deposition (MOCVD) and molecular beam epitaxy (MBE) have become important crystal-growing technologies for high-speed devices and lasers during the past fifteen years, but they have yet to demonstrate the cost-effectiveness needed for high-volume LED production.

AlGaAs LEDs can be grown using MOCVD, but 650-nm red devices made with this technology have a quantum efficiency that is substantially less than that of LPE-grown devices. AlInGaP devices will probably require MOCVD. VPE can not be used because it requires aluminum-bearing
compounds, such as AlCl, which attack the quartz walls of the reactor. LPE is an unlikely candidate because maintaining adequate composition control is difficult when LPE is used.

An LED chip must do a good job of converting electrons to photons (that is, it must have a high internal quantum efficiency) and must be designed so the photons can be easily extracted from the chip (it must have a high extraction efficiency). High internal quantum efficiency requires a material with a low defect density and a device structure that efficiently injects minority carriers into the active region of the device. The material requirements of LEDs are more stringent in some ways than those of lasers because LEDs operate at relatively low current densities. Lasers typically operate at densities an order of magnitude higher than those of LEDs. Consequently, they can often tolerate substantially higher concentrations of defects because the injected carriers saturate the defects and prevent them from having much effect on laser performance.

A typical LED device consists of a chip approximately 250 x 250 x 250 µm in size that is mounted in a reflective cavity on a metal lead frame and encapsulated in clear epoxy (Fig. 2a). The epoxy serves as a structural element to hold the lead frame together, as a lens to focus the light, and as an index-of-refraction-matching medium that allows more light to escape from the chip.

Various types of epitaxial structures are used for LEDs (Fig. 2b-d). GaAsP:N devices are diffused homojunction devices in which Zn is diffused into an n-type epitaxial layer. High-performance AlGaAs and AlInGaP devices are grown-junction double heterostructures. A heterostructure enables the efficient injection of carriers into the active region of the device and allows the confining layers to be transparent to the generated light, which makes a high extraction efficiency possible.

Lattice matching, where the substrate and epitaxial layers have the same atomic spacing, is a key issue in the growth of high-quality materials and in the formation of heterostructures. Any composition of AlGaAs is nearly lattice-matched to GaAs substrates, a major advantage for this technology that facilitates the growth of high-quality complex structures. AlInGaP can be lattice matched to GaAs, but the percentage of indium must be precisely controlled. Consequently, this alloy is much more difficult to grow and control than is AlGaAs. The older GaAsP:N technology is not matched to either GaAs or GaP substrates, so high defect levels are inevitable even when compositional grading layers are utilized. Heterostructures are not feasible in this system.

GaP:N and GaP:Zn,O are lattice-matched to their GaP substrates but, like GaAsP:N, they are indirect-bandgap semiconductors that have lower internal quantum efficiencies than direct-bandgap semiconductors. In indirect semiconductors (including silicon and germanium) the majority of the electrons, which concentrate in the minimum energy regions of the conduction band, have a different momentum than the holes (the positive charge carriers). The holes concentrate in a region of the valence band in which they have nearly zero momentum. Consequently, radiative recombination (recombination of an electron and a hole that results in the production of a photon) is “forbidden.” This is so because the emission of a photon would violate the principle of conservation of momentum, which demands that the total momentum of the electron and hole be equal to the momentum of the photon. The photon has nearly no momentum, so radiative recombination is only allowed when the momentum of the electron can be balanced by that of the hole, which is not the case here. In direct semiconductors, on the other hand, most of the electrons and holes have a momentum that is nearly zero, and radiative recombination can be very effi-
cient in high quality crystals having low levels of defect-related "shunt" paths that generate heat. AlGaAs and AlInGaP are direct-bandgap semiconductors for the alloy compositions used to make high-brightness devices.

The transition from direct to indirect bandgap with increasing aluminum concentration limits AlGaAs to red emission and makes green AlInGaP devices less efficient than yellow and red ones. Indirect semiconductors, such as GaP, are inherently inefficient light emitters. The addition of nitrogen gives them a "quasi-direct" recombination path, but they still have an internal quantum efficiency that is an order of magnitude or more lower than the best efficiency available from direct semiconductors, which approaches 100 percent.

High light-extraction efficiency depends on good current-spreading across the top of the chip, which minimizes light loss under the ohmic contact. In addition, the diode's layers must be relatively thick so that a

3. External quantum efficiency as a function of peak emission wavelength for AlInGaP devices. For red and yellow wavelengths beyond 590 nm, the devices have 5 percent efficiency. The efficiency drops at shorter wavelengths due to the approaching transition from a direct to an indirect semiconductor. The CIE eye-response curve is also shown.

<table>
<thead>
<tr>
<th>LED TYPE (Peak Wavelength)</th>
<th>COLOR</th>
<th>PRODUCTION METHOD</th>
<th>STRUCTURE*</th>
<th>BANDGAP TYPE</th>
<th>LATTICE MATCHED</th>
<th>TYPICAL EXTERNAL QUANTUM EFF. %</th>
<th>TYPICAL PERFORMANCE (lumens/watt)</th>
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<tbody>
<tr>
<td>GaAsP</td>
<td>Red(650)</td>
<td>VPE + Diffusion</td>
<td>HJ</td>
<td>Direct</td>
<td>No</td>
<td>0.2</td>
<td>0.15</td>
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<td>GaP:Zn O</td>
<td>Red (700)</td>
<td>LPE</td>
<td>HJ</td>
<td>Indirect</td>
<td>Yes</td>
<td>2</td>
<td>0.4</td>
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<tr>
<td>GaAsP:N</td>
<td>Red (530)</td>
<td>VPE + Diffusion</td>
<td>HJ</td>
<td>Indirect</td>
<td>No</td>
<td>0.7</td>
<td>1</td>
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<td>GaAsP:N</td>
<td>Yellow (585)</td>
<td>VPE + Diffusion</td>
<td>HJ</td>
<td>Indirect</td>
<td>No</td>
<td>0.2</td>
<td>1</td>
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<tr>
<td>GaP:N</td>
<td>Yellow-Green (565)</td>
<td>LPE</td>
<td>HJ</td>
<td>Indirect</td>
<td>Yes</td>
<td>0.4</td>
<td>2.5</td>
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<tr>
<td>GaP</td>
<td>Pure Green (555)</td>
<td>LPE</td>
<td>HJ</td>
<td>Indirect</td>
<td>Yes</td>
<td>0.1</td>
<td>0.6</td>
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<td>LPE</td>
<td>SH</td>
<td>Direct</td>
<td>Yes</td>
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<td>2</td>
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<tr>
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<td>Red (650)</td>
<td>LPE</td>
<td>DH</td>
<td>Direct</td>
<td>Yes</td>
<td>8</td>
<td>4</td>
</tr>
<tr>
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<td>Red (650)</td>
<td>LPE</td>
<td>DH-TS</td>
<td>Direct</td>
<td>Yes</td>
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<td>8</td>
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<tr>
<td>AlInGaP</td>
<td>Orange (620)</td>
<td>MOCVD</td>
<td>DH</td>
<td>Direct</td>
<td>Yes</td>
<td>6**</td>
<td>20**</td>
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<tr>
<td>AlInGaP</td>
<td>Yellow (585)</td>
<td>MOCVD</td>
<td>DH</td>
<td>Direct</td>
<td>Yes</td>
<td>5**</td>
<td>20**</td>
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<tr>
<td>AlInGaP</td>
<td>Green (570)</td>
<td>MOCVD</td>
<td>DH</td>
<td>Direct</td>
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<td>6**</td>
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<td>SIC</td>
<td>Blue (480)</td>
<td>MOCVD</td>
<td>HJ</td>
<td>Indirect</td>
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</table>

* HJ Homojunction
SH Single Heterostructure
DH Double Heterostructure
DH-TS Double Heterostructure, transparent epitaxially-grown substrate
** Best reported results [9]. Typical commercial performance not established.
high proportion of the light can be extracted from the sides of the chip rather than being internally reflected to the substrate and absorbed there. Ideally, the substrate should also be transparent, enabling downward-traveling light to bounce off of the back of the chip and ultimately escape. GaAs:P devices are grown on a transparent GaP substrate, and the highest-performance AlGaAs device structure also has a "transparent" substrate. This substrate is actually an epitaxial layer grown thick enough (100-200 µm) to allow the absorbing GaAs substrate to be removed.

AlInGaP devices are grown on an absorbing GaAs substrate, and growing AlInGaP thick enough to permit removal of the GaAs layers it is not yet viable. A thick, transparent, highly conductive window layer is required, but p-type AlInGaP has a relatively low conductivity. The solution found to date is a GaP window layer grown on top of the AlInGaP heterostructure [8,9]. Devices of this type exhibit excellent quantum efficiency and luminous performance (Figs. 3, 4). The GaP window layer is mismatched relative to the AlInGaP heterostructure, but the defects formed at the AlInGaP interface do not appear to propagate downward and degrade the device performance. GaP has the advantage of relatively high conductivity compared to AlInGaP and can be readily grown and controlled. The device performance shown in Figs. 3 and 4 was achieved using 45-µm-thick GaP window layers and represents the best-known performance for AlInGaP LEDs for all colors from red through green.

It should be possible to improve the efficiency further by making the layer even thicker and by adding a Bragg reflector at the base of the epitaxial structure to reflect downward-traveling light back up into the epitaxial structure, giving it a chance to escape.

AlGaAs has also been utilized as a window material. It is lattice-matched and has high conductivity, but it absorbs in the yellow and green spectral regions. The best of these devices used 7-µm-thick AlGaAs windows and emit at 620 nm. They have about one quarter the efficiency of the thick-GaP window devices shown in Figs. 3 and 4.

Future Developments

We expect red-emitting AlGaAs and orange- and yellow-emitting AlInGaP to be used in areas where high flux or reduced power consumption is required. These include automotive, moving-message panel, and battery-powered applications. Green AlInGaP devices are more than twice as bright as existing GaP:N green devices and should also prove to be important devices.

AlInGaP technology is still at an early stage of development, so we expect further improvements in performance, particularly for green devices. In the long term, red-orange (~620-nm) AlInGaP devices will compete with AlGaAs for many red-emitter applications, and AlInGaP may well become the dominant high-performance LED technology for all colors from red through green.

The cost relative to existing technology will be important in determining the timing and extent of AlInGaP's penetration into most applications. A key issue will be developing a robust, high-volume production technology comparable to the existing GaAs:P and GaP technologies. This challenge is formidable. As a result, AlInGaP technology will probably evolve over the next five to ten years. We expect older LED technologies to continue to grow and be utilized for the majority of applications where cost sensitivity is a key issue and higher performance is not essential.

The future direction of blue-emitter technology is less clear. SIC, today's main commercial technology, can be expected to continue to improve. But performance comparable to AlGaAs and AlInGaP cannot be expected because the latter are direct-bandgap semiconductors while SIC has an indirect bandgap. ZnSe is a direct-bandgap semiconductor with a large enough bandgap to make blue emitters. Recent ZnSe injection-laser results prove that relatively high internal quantum efficiencies can be achieved in ZnSe, so blue LEDs with external efficiencies comparable to AlGaAs and AlInGaP are conceivable. However, major technical issues related to reliability, drive voltage, and extraction efficiency remain to be resolved. As this article was being written, no room-temperature ZnSe devices with performance exceeding 1.0 lumens/watt had been reported, although quantum efficiencies as high as 1 percent at 77 K and 0.1 percent at room temperature have been reported [13].

GaN, AlGaN, and AlInGaN are other direct-bandgap semiconductors capable of blue emission [14]. GaN devices have been announced commercially, although their performance is no better than the best SIC devices. Injection lasers have not been fab-

4. LED luminous performance versus wavelength for AlInGaP compared to other LED technologies. Luminous performance is the product of power efficiency (roughly equal to quantum efficiency), and the eye’s response.
Fabricated in the GaN system.

In summary, the performance of AlGaNAs has enabled LEDs to penetrate markets requiring high flux and/or low power consumption. AlInGaP technology, which yields high performance from red-orange to green, is expected to accelerate the use of LEDs in new applications. Blue devices are emerging, and recent ZnSe developments suggest that blue performance comparable to AlGaNAs and AlInGaP may be possible, but the timing is uncertain. Developing an adequate blue device would permit the fabrication of full-color, large-area, sunlight-viewable, flat-panel displays.

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