

UV-C Light Emitting Diodes

By Craig Moe

Ultraviolet (UV)-LEDs have rapidly improved as they have entered the commercial market, with sales totalling \$45 million out of the total \$495.4 million UV lamp market in 2012.¹ The majority of the market is currently served by products emitting in the UV-A wavelength range, with curing being the largest application. UV-C-LED technology is improving rapidly as commercialization has begun, with large markets in water purification and disinfection driving

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advances. This article discusses the technology behind UV-LEDs and how advances in the UV-C range can complement longer wavelength curing applications.

UV-LEDs are manufactured from a class of materials referred to as III-V semiconductors. These materials are epitaxially grown into crystals with a precise ratio of one atom from the Group V column of the periodic table to one atom from the Group III. The smaller the atomic number of the elements used, the more ionic the character of the atomic bonds, resulting in a smaller lattice constant and larger electrical bandgap. This bandgap determines the wavelength at which a particular material will emit light. This ability to tailor by alloying and the fact that many III-V semiconductors are direct bandgap is responsible for the fact that the

majority of the optoelectronics in use today are constructed from III-V materials.² For example, the mature technologies of lasers used in fiber-optic communications are fabricated from indium gallium arsenide phosphide and are designed with specific alloying ratios to emit at wavelengths of 1.3 μm or 1.55 μm , while the laser in a commercial DVD player has an active region of gallium indium phosphide and emits at 650 nm.

The nature of III-phosphide and III-arsenide materials is such that optoelectronic structures with alloys of specific concentrations can be designed so that the entire material stack has the same crystal lattice constant or spacing between atoms. This, in conjunction with the ready availability of near-perfect substrates of gallium arsenide and indium phosphide, allows for defect-free optoelectronic devices to be produced. Any defect in the crystal structure is a point where electrical carriers can recombine in a way that does not produce the desired wavelength and, thus, the efficiency is reduced. It is because of these native substrates and careful epitaxial growth of optoelectronics that much of the technology we use today is possible.

Up until the early 1990s, the shortest wavelength, commercially available III-V light-emitting diodes were a weak green—suitable primarily for telephone backlighting and indicator lights. They were made from aluminum gallium phosphide. It wasn't until Shuji Nakamura³ and others

successfully produced LEDs of indium gallium nitride that blue and true green LEDs (and later solid-state lasers) in these wavelengths were realized.

Unlike their longer wavelength counterparts, there were no native substrates available to use in producing these devices. Epitaxial structures were instead produced on foreign substrates, such as sapphire and silicon carbide. Due to the large lattice mismatch between these materials, the resulting epitaxy had a large number of defects, as many as 10^{10} per square centimeter. While this would make light generation impossible in phosphide or arsenide materials, a unique property of the III-nitrides makes LEDs of this quality reasonably efficient in this material.

Numerous improvements in this field have steadily increased the output power and efficiency of blue LEDs, which (in conjunction with phosphors to convert the short wavelength into white light) has launched the revolution in solid-state lighting that is projected to save 1,488 terawatt-hours from 2010 to 2030.⁴

By using aluminum instead of indium in the nitride alloys, shorter UV wavelengths can be produced from solid-state emitters. The output wavelength is dependent on the ratio of aluminum, gallium and indium used. The emitting wavelength of gallium nitride is near 365 nm. UV wavelengths longer than this (most of UV-A) use InGaN in the active region and are, for the most part, grown on sapphire substrates like their visible brethren—although some very high-power LEDs use more expensive GaN substrates. This similarity to visible emitters allows manufacturers to take advantage of the tremendous amount of development poured into solid-state lighting, and it is for this reason that UV-A-LEDs are the most mature and reliable of UV solid-state emitters.

Below 365 nm, aluminum gallium nitride becomes the active medium for UV emission. For wavelengths as short as roughly 340 nm, GaN substrates or GaN-on-sapphire templates can still be used without a significant increase in crystal defects. Below this, however, most commercial LEDs use sapphire substrates with aluminum nitride or aluminum gallium nitride buffer layers. The films are generally more defective than their GaN counterparts due to

the lower mobility of the aluminum adatom during growth. While AlGaN with dislocation densities on the order of 10^8 cm⁻² are obtainable with sophisticated epitaxial processes, this remains expensive, while the output power and reliability of the resulting LEDs appear to still be limited by a high defect density. However, using an AlN substrate allows for device layers to be pseudomorphically grown without introducing new defects,

FIGURE 1

Histogram of LEDs run for 1,000 hours at 100 mA without hermetic packaging

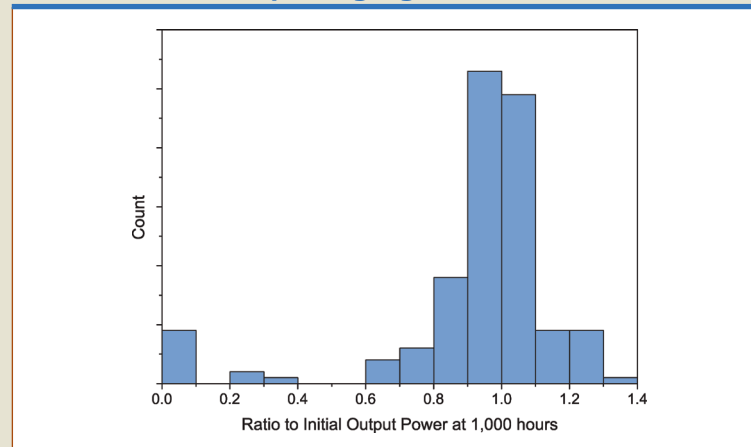
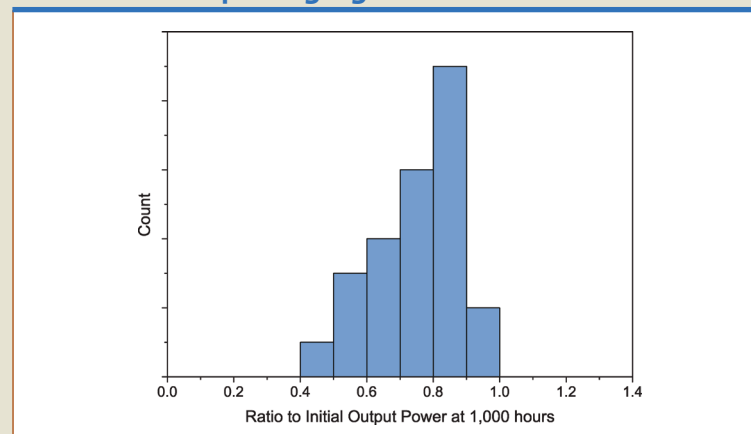


FIGURE 2

Histogram of LEDs run for 1,000 hours at 100 mA with hermetic packaging



producing LEDs with dislocation counts less than 10^6 cm^{-2} . It is for this reason that the highest power, most reliable devices in the mid-UV will come from AlN substrate technology.

The shortest wavelength III-nitride LED produced consisted almost entirely of aluminum nitride and emitted at 210 nm.⁵ This, however, was only a proof of concept and emitted very little light. Currently, the nature of the dopants used to produce carriers in AlN and AlGaN is such that the wavelength limit of commercializable UV-LEDs is around 235 nm.⁶ In general, the efficiency of an LED decreases as one moves deeper into the UV. Some of this is due to the material challenges of working with aluminum gallium nitride, as the dopant species that provide carriers requires more energy to activate. However, the lack of research funding into the mid-UV is also a contributing cause. When the Defense Advanced Research Projects Agency funded a two-year program to increase power output and efficiency in wavelengths below 280 nm, a large improvement was achieved in the targeted wavelengths, pushing external quantum efficiencies to more than 5%.

The ideal emission wavelengths for LEDs produced on AlN templates and substrates range from 250 to 290 nm. Below these wavelengths, significant research is needed to mitigate the low electrical conductivity of high aluminum composition AlGaN, and low quantum efficiency of the devices. Above about 300 nm, the lattice mismatch between the corresponding AlGaN layers and the underlying aluminum nitride makes it difficult to produce epitaxial structures without introducing an increased number of crystal lattice dislocations.

Crystal IS has successfully produced low-defect density AlN substrates for mid-UV-LEDs. The optoelectronic

FIGURE 3

Light output versus input current for 268 nm Crystal IS LEDs tested by the U.S. Army Research Laboratory⁷

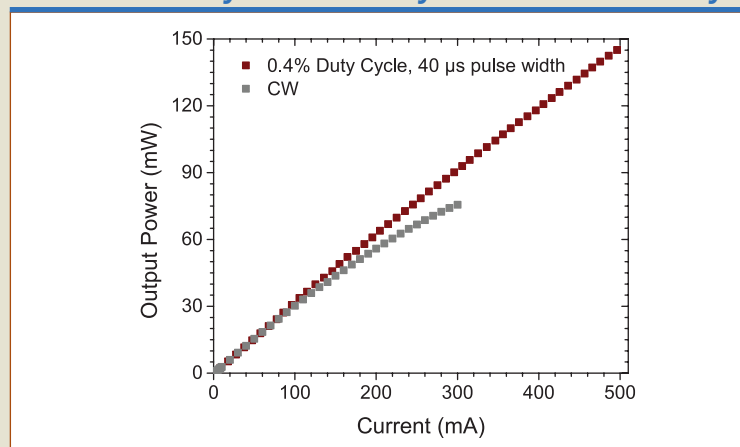
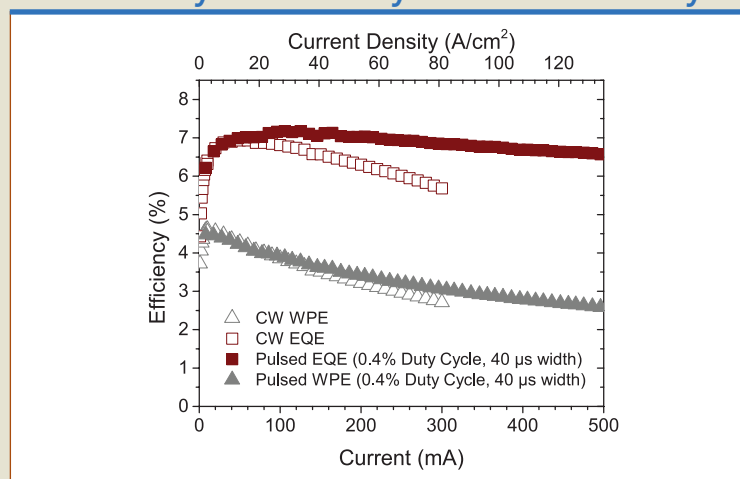


FIGURE 4

Efficiency versus input current for 268 nm Crystal IS LEDs tested by the U.S. Army Research Laboratory⁷



AlGaN structures epitaxially grown on these are pseudomorphically strained to the substrate, producing no additional defects through the active region. This defect reduction both improves the wall-plug efficiency of the LEDs and reduces the heat generated in the chip, which, in turn, reduces the output power degradation both in the short term as the device achieves thermal equilibrium and the

longer term. UV-C-LEDs grown on AlN substrates show a lower thermal derating than even UV-A-LEDs on sapphire substrates, while a test of 170 UV-C-LEDs fabricated over the course of six months showed a median degradation of less than 4% after 1,000 hours of continuous operation at 100 mA. Hermetically sealing the LED in a TO-39 package further eliminated catastrophic failures. (Figures 1 and 2)

FIGURE 5

Light output versus input current for 278 nm Crystal IS LEDs tested by the U.S. Army Research Laboratory⁷

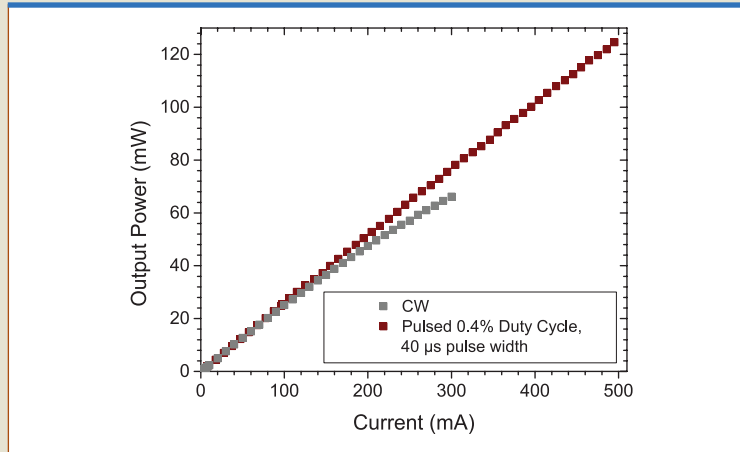
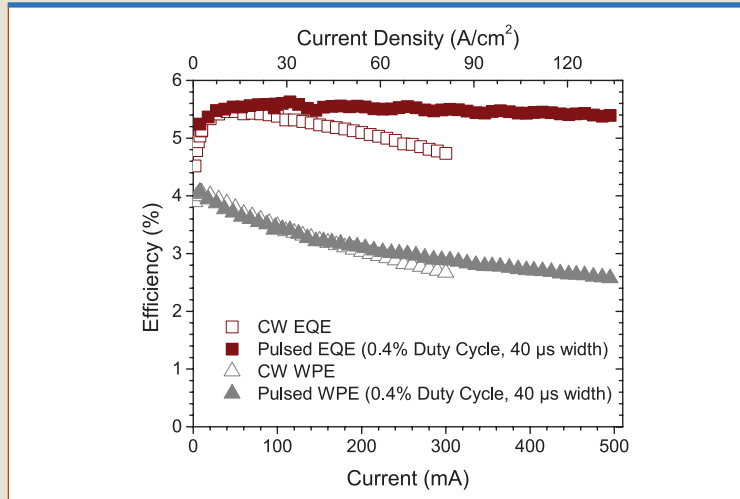


FIGURE 6

Efficiency versus input current for 278 nm Crystal IS LEDs tested by the U.S. Army Research Laboratory⁷



A key efficiency limitation in UV-LEDs is managing the light output—both in extracting the light from the AlGaIn layers from which it is generated and directing the light to the desired surface in a uniform manner. Many light extraction techniques have been developed for visible LEDs to use in solid-state lighting applications. These are both more difficult and more

critical to use with UV-LEDs as the index of refraction difference between the III-nitride material and the air increases with increasing bandgap, resulting in greater internal reflection at the interface and less light extraction. Crystal IS has increased the extraction efficiency of our LEDs from 2.5% on-wafer to 15% through thinning the AlN substrate after

fabrication and the use of a UV-transparent encapsulant.

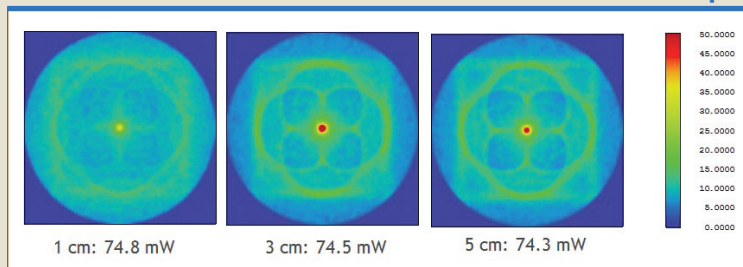
These extraction improvements coupled with improvements in the epitaxial structure of the device has allowed Crystal IS to achieve high output powers from a single LED on an 820 μm by 820 μm chip with an active area of 0.37 mm^2 . Figures 3-6 show the light output versus current for devices emitting at 268 and 278 nm under both continuous and pulsed operation as measured by the U.S. Army Research Laboratory. The two current input methods diverge only slightly beginning above 150 mA as device self-heating begins to limit the output power of the continuously driven LED. This shows in the external quantum efficiency (the ratio of the extracted photons to the injected carriers) and wall-plug efficiency (the ratio of the optical power emitted to the input electrical power) where the efficiency loss due to heating is between 9 and 15%.

Note that the conditions for pulsed operation (40 μs pulses and a 0.4% duty cycle) result in the device being turned on and off 100 times a second. This is only possible due to the solid-state nature of the LED and its instant turn-on. LEDs have been run in this mode for thousands of hours with no increase in degradation over continuously driven devices. This greatly extends the lifetime in a real-world usage scenario, where the LED needs to only be in operation when the application calls for it, as opposed to the long warm-up times of traditional UV lamps.

The final challenge is to evenly distribute the generated UV light across the desired area. As the primary application looks to be water purification, this distribution becomes extremely important to avoid dead spots where untreated water might slip through. Crystal IS has done significant

FIGURE 7

Computer modeling displaying cross sections of a 3.1 cm diameter, 10 cm long Teflon-coated tube irradiated with five 15 mW UV-LEDs at each endcap



modelling of flow cells and, through careful choice of materials and LED configuration, has demonstrated a 5 mW/cm^2 minimum exposure across a 10 cm long, 3.1 cm diameter tube with five LEDs each emitting 15 mW in power, as shown in Figure 7.

Similar principles can be applied to curing applications where a UV-C-LED would work in conjunction with a longer wavelength UV-A light source. The shorter penetration depth of UV-C would be ideal for surface curing of paints and inks, which is currently a weak point in single-wavelength UV-curing solutions. This would require optimized photoinitiators which are currently being developed for a wide range of wavelengths in the UV spectrum. The large markets projected in air and water disinfection will help drive cost per milliwatt down for UV-C-LEDs, possibly making them a cost-effective alternative.

Conclusion

UV-C-LEDs on aluminum nitride substrates are making great strides in output power, reliability and cost effectiveness, and look to be a solution which complements UV-A-LEDs for curing applications. The combination of other markets in air and water disinfection and the inherent material

problems in longer UV wavelengths leads us to believe that UV-C-LED performance will exceed that of UV-B for the near future. ▀

Acknowledgements

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