

UV-LED Overview Part III: Diode Evolution and Manufacturing

By Jennifer Heathcote

This article is the third installment in a three-part series designed to consolidate key principles and technical information regarding the science and engineering behind UV-LEDs. If you have not read “Part I—Operation and Measurement” (July/August 2010) or “Part II—Curing Systems” (Sept/Oct 2010), you may want to do so before continuing with Part III.

Light Emitting Diodes (LEDs) are engineered to produce discrete infrared, visible or ultraviolet (UV) wavelengths when a DC voltage is applied. The type of output, overall performance and operating efficiency of any given die is directly related to its material composition and the manufacturing methods employed. As a result, there has been a concerted

trying to understand and optimize the core technology as well as implement reliable manufacturing methods. The purpose of this paper is to provide a general history of LED development as well as an overview of typical processes employed in chip production. It is only with an understanding of how far the technology has come, as well as what is involved in producing LED emitters, that one can truly appreciate the potential of where the technology has yet to take us.

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effort for the last 60 years to identify new semiconductive compounds, improve chip structures and optimize processing techniques. Much of this activity has been concentrated in the longer wavelength visible and infrared ranges; and has directly led to improved yield rates, lower power consumptions, brighter colors and increased operating efficiencies as well as a steady decline in unit costs.

By comparison, UV-LED technology is relatively new, and engineers and developers are still hard at work

Discovery of Electroluminescence

Jöns Jacob Berzelius (1779-1848) was a successful Swedish scientist recognized for his great achievements in the field of electrochemistry. His penchant for methodical experimentation led to his discovery of previously unknown elements, including cerium, selenium and thorium. In 1824, while attempting to artificially manufacture diamonds, Berzelius synthesized Silicon Carbide (SiC). Silicon Carbide is a strong and chemically inert material having low density, high surface hardness and minimal thermal expansion.

Seven decades after the invention of Silicon Carbide, a Pittsburgh-based

American entrepreneur, Edward Goodrich Acheson (1856-1931), developed a low-cost, high-volume manufacturing process to produce the material. Acheson was granted a patent for his process in 1893 and subsequently marketed the material to the abrasives and grinding industries under the trademark of Carborundum.

In the early 1900s, the British-based Marconi Company sent a young electronics engineer by the name of Henry Joseph Round (1881-1966) to America to research developments in radio technology. One of Round's projects involved the evaluation of Carborundum and its use in early crystal-detector radios. Round subjected Silicon Carbide crystals to various experiments, including ones in which he applied a direct current to the material. He noticed that whenever a current was applied, the crystals emitted light. This was the very first observation of electroluminescence. Round's findings were published in the Feb. 9, 1907, edition of the journal *Electrical World*.

In 1928, a Russian scientist, inventor and radio technician by the name of Oleg Losev reported his own electroluminescence observations. He conducted a series of experiments on Silicon Carbide rectifiers used in radio circuits and discovered that the light emissions could be switched very quickly. Losev believed that the phenomenon could be further developed for use as a light relay. He is credited with being the first individual to envision a practical application for electroluminescence.

It wasn't until the late 1960s that the first LEDs made from Silicon Carbide became available. The devices emitted a blue spectral output but had a poor 0.005% electrical-to-optical power-conversion efficiency. Despite all the best efforts and technological advancements, pure Silicon Carbide

diodes emitting at 470 nm never exceeded 0.03% efficiency. As a result, the use of Silicon Carbide in the production of LEDs was mostly abandoned in the 1990s for better performing and more efficient compounds. In more recent years, SiC is once again being used in conjunction with more complex alloys to produce regular and high-brightness visible LEDs.¹

Evolution of LED Semiconductor Compounds

In the decades following the discovery of electroluminescence, researchers identified and evaluated many naturally occurring semiconductive materials. By the 1950s, the general consensus was that any serious advancement in the technology would require the development of new man-made compounds. These compounds would be engineered to embody specific electrochemical and emissive properties; operate at higher efficiencies; and consume less power. An entire portfolio of new materials was necessary with the diode performance determining which compounds would be used for which applications.

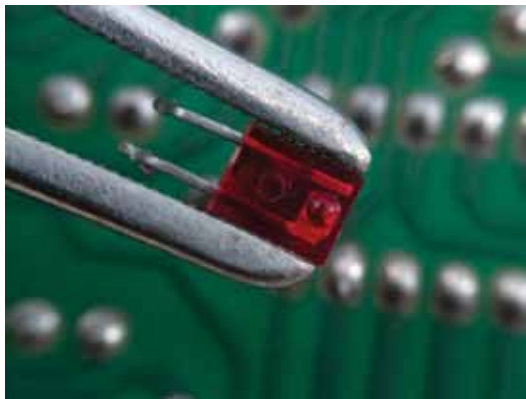
Formal research and development projects involving LED semiconductors started in the 1950s in the labs of Radio Corporation of America; General



Nick Holonyak, Jr., "father" of the Light Emitting Diode.

Electric; International Business Machines; American Telephone and Telegraph; Monsanto and Hewlett-Packard, as well as in the labs of various universities. From these efforts, the first infrared (870-980 nm)-emitting LEDs based on Gallium Arsenide (GaAs) were reported in 1962. Nick Holonyak, Jr., who was consulting at GE, is given credit for the invention and is affectionately known as the "father of the light emitting diode." Texas Instruments became the first company to use a small volume of these diodes commercially at a reported price of \$130 each.¹ Due to technical advancements, infrared LEDs now yield a unit price that is miniscule in comparison to what Texas Instruments initially paid. As a result, infrared LEDs are extensively used in video games, remote controls and communication systems.

After the initial successes with Gallium Arsenide infrared LEDs,



Modern versions of red LEDs.



development projects quickly expanded to include Aluminum Gallium Arsenide (AlGaAs) and Gallium Arsenide Phosphide (GaAsP). By 1967, the first visible-spectrum, red emissions were produced by a team at IBM using AlGaAs. IBM soon integrated red LEDs made with GaAsP into circuit boards and mainframe computers as status and function indicators. Modern versions of the devices are shown on page 2. In the 1960s, General Electric became the first company to commercially sell red LEDs at a price of \$260 each.¹ In an effort to reduce costs, Monsanto focused on manufacturing and opened a dedicated facility in 1968 to begin high-volume production.

Research expanded to Gallium Phosphide (GaP) in the hopes of making more efficient red and green LEDs. AT&T utilized green LEDs in the late 1970s for backlighting touch-tone phone keypads. They selected red LEDs for use as status indicators for multiline office phones. Hewlett-Packard and Texas Instruments developed GaAsP LEDs for the alphanumeric displays in digital calculators and watches. Monsanto continued experimenting with various manufacturing techniques and managed to achieve emissions in the red, orange, yellow and green spectrums. While electronics applications utilizing LEDs progressively expanded, there remained various challenges regarding low diode efficiencies, limited brightness, high power consumption and the inability to view LED emitters in direct sunlight.

In a much more forward thinking pursuit, the director of the Materials Research Division at RCA was intrigued by the possibility of a flat screen television where red, green and blue LEDs would be instantly switched in various combinations to create video images. At the time, red and green



Message-changing highway billboard with red, green and blue high-brightness LEDs.

LEDs were actively being developed from AlGaAs, GaAsP, GaP and GaAsP; however, the industry had not yet determined the optimal structure for blue emitters. Gallium Nitride (GaN) was thought to be the best candidate and in the late 1960s RCA began working on the development of blue LEDs made from this material. RCA made its first observations of GaN luminescence centered at 475 nm in 1971. Additional doping of the material with magnesium generated 430 nm blue and violet LEDs.

Despite some initial success, RCA's management team became discouraged by the lack of commercially viable progress and the magnitude of additional research required. RCA terminated its work on Gallium Nitride in the mid-70s. Even today, 40 years after RCA embarked on its quest to develop a flat screen television made entirely of LEDs, the dream of an all LED television is still a bit elusive. While red, green and blue LEDs are widely used for large, electronic highway billboards and commercial signage, LEDs are limited to indicator lights and high-brightness backlighting in all general consumer flat screen televisions. See photos above.



LED-backlit Liquid Crystal Display (LCD) television.

Fortunately for the UV-curing industry, work on GaN was resurrected by Japan in the 1980s. In 1989, Japanese researchers produced the first GaN junction with magnesium doping and in 1992 a GaN UV-LED with an efficiency of around 1% was born. The Nichia Chemical Industries Corporation in Japan has been a leading driver of development using GaN, GaInN and GaP compounds doped with impurities to produce high-brightness blue, green, white and UV-LEDs. Commercially, Gallium Nitride LEDs are most widely used for backlighting electronic devices such as mobile and smart phones; personal data assistants; and global positioning systems. High-brightness LEDs are increasingly being used in automotive applications; traffic and pedestrian crossing signals; backlighting of LCD and rear projection television displays; and general lighting.

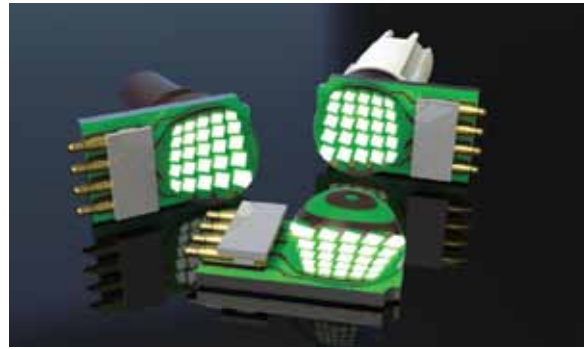


High-brightness LED traffic signal (left) and crossing signal (right).

Development work has also continued on AlGaInP high-brightness LEDs in the rest of the visible spectrum. Alloys of these are now the dominant materials used for high-brightness emissions in the red (625 nm), orange (610 nm) and yellow (590 nm) spectral range. It should be emphasized that UV-LEDs packaged for use in curing systems still represent a very small portion of the total volume of UV, white and high-brightness LEDs; however, since the technologies are similar, the design and manufacturing of UV-LED chips directly benefits from improved performance and higher volume production of white and high-brightness diodes. Examples of common high-brightness LED

applications are shown at left while various packages of UV-LED chips are provided in the photos to the right.

Despite the negligible peak irradiance of the first UV-LED chips (1992), the discovery was a significant breakthrough in the evolution of semiconductor technology as it confirmed that LEDs were not limited to infrared and visible spectrums. As is the case with most cutting edge technologies, it often takes years or decades to transition from initial discovery to viable application. The evolution of UV-LEDs has been no different. It took more than a decade after the first lab-created ultraviolet diode for UV-LED systems to begin appearing on the market (2003). The early systems were not very powerful and the applications were limited. Fortunately, the overall output, performance and efficiencies have increased every year. Starting around 2008, UV-LED systems began generating sufficient UV output at a reasonable price point to make UV-



Packaged UV-LEDs from Integration Technology (top), Nichia (bottom).

LED curing systems commercially viable for an increasing number of applications.

UV Process Supply and Phoseon are credited with commercializing the first UV-LED systems. Other companies such as Integration Technology Limited, Lumen Dynamics, Summit UV, Sun LLC and Clearstone, to name a few, entered the market soon afterward. Today, the majority of conventional UV system developers have embarked on some level of research or commercialization of irradiators made with UV-LEDs. Large



High-brightness Formula One rain tail light (left) and high-brightness headlight (above) are examples of common high-brightness LED applications.

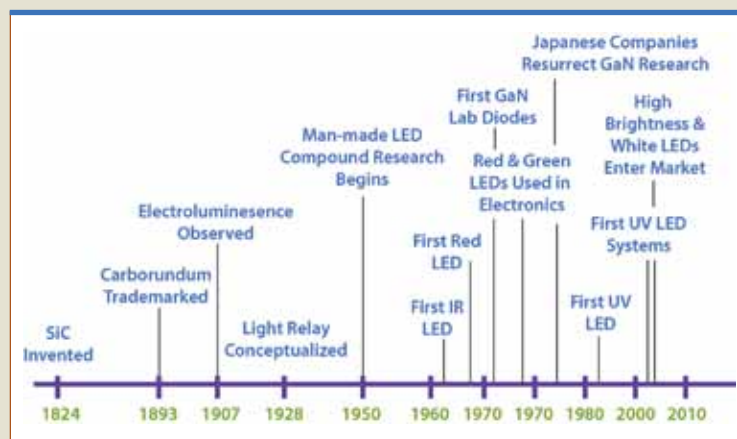
investments are being made despite the reality that not all applications are currently suited for UV-LED curing and many system configurations are still quite expensive. In lieu of these challenges, the overall chip and packaging technology continues to evolve and, in time, prices and performance will also improve. This has encouraged more semiconductor manufacturers, chip packaging companies and UV system developers to enter or consider entering the market. This increase in competition will likely advance the technology much further in a much shorter period of time.

To summarize, engineers and research scientists have been formulating and experimenting for nearly 60 years with an ever increasing portfolio of man-made semiconductor compounds that emit infrared, visible and, most recently, ultraviolet wavelengths. These compounds have been engineered to embody specific electrochemical and emissive properties while operating at increasingly higher efficiencies and consuming less power. Since each compound emits a different wavelength and/or amount of energy, an entire portfolio of materials is necessary in order to produce dies for various applications. The final diode performance determines which compounds are used for which applications.

It should be emphasized that the necessary research is far from exhausted, and there are presently complex alloys still in development, including GaN/SiC, GaN/Sapphire, GaN/Silicon, GaN/B-Si/pSiC, GaN Glass, GaN/ZnO, GaN/AlN, GaN/B-GaN/pAlN and GaN/Ge, to name a few. Very preliminary research into materials that emit shorter wavelength UV-A, UV-B and UV-C diodes is also currently underway. A timeline summarizing key breakthroughs in development since the discovery of the first semi-

FIGURE 1

Timeline for evolution of LEDs



conductive compound, Silicon Carbide (SiC), is illustrated in Figure 1.

Semiconductor Manufacturing

The spectral emission, electrical-to-optical power-conversion efficiency, unit cost, quality, yield rate and lifetime hours of each die depend not only on the substrate material, but also on each additional processing step and manufacturing method employed. As a result, significant investment has gone into developing and controlling the production of LEDs.

Actual manufacturing yield rates vary significantly depending on the type of LED. Yield rates for standard infrared and visible LEDs have improved drastically over the past 50 years as most of the production issues have been resolved. Yield rates for white and visible spectrum high-brightness LEDs are increasing rapidly; although, there is still room for improvement. The current quality of UV-LED production, unfortunately, is not very good and much optimization work remains to be done. With UV-LEDs, there is a significant amount of scrap generated during production that has a direct impact on the final die cost and performance.

Every single stage and step of the production process—from raw material selection through to packaging—is critical. Each has the potential to introduce defects or foreign matter, resulting in lower efficiencies and insufficient performance in the final dies. As a result, numerous quality assurance checks are performed and most processes take place in Class 1 and Class 10 clean rooms. Each and every step of the manufacturing process, therefore, is a distinct and challenging engineering and quality improvement project that takes years, if not decades, to perfect.

An overly simplified description of this process can be segmented into three parts that focus on the ingot, wafer and die. It should be noted that there are many variations to the production methods described; not all steps have been included in this document; and each manufacturer likely incorporates proprietary processing that is not generally known to the public. As a result, the following sections are meant to give the reader some general insight into a typical LED manufacturing process and are by no means meant to be fully comprehensive.

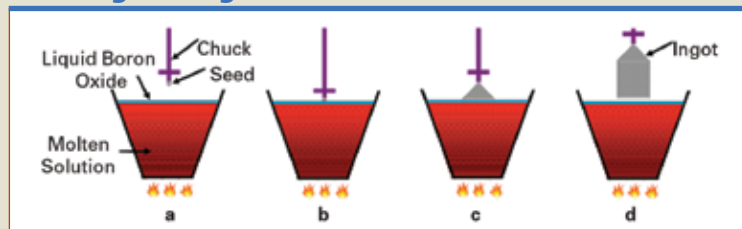
The Ingot

The manufacture of LED semiconductors starts with the production of a long, cylindrical ingot, also called a boule. The ingot is typically formed to diameters of 2, 4, 6, 8 or 12 inches and can be grown to any desired length. The material properties are uniform throughout the ingot, and the crystalline structure contains relatively few impurities or contaminants. This is achieved through precision temperature and pressure control in a clean environment and by using only the highest purity of raw materials.

Formation of the ingot begins when high-grade raw materials are mixed together in a specially designed reactor

FIGURE 2

Forming the ingot



chamber as illustrated in Figure 2. When elevated temperatures and pressures are applied, the materials combine to form a uniform molten solution that is covered with a layer of liquid boron oxide to prevent vaporization. A rod or chuck is then lowered toward the solution (2-a). On the end of the chuck is a tiny, purified seed that contains the exact properties of the mixture. When the seed reaches the solution, a chemical bond begins to form between the seed and the molten material (2-b).

As the rod is rotated and withdrawn at a slow and constant rate of speed, some of the mixture begins to cool and solidify on the seed. The top of



Fully formed ingots.

the ingot takes the shape of a cone that tapers from the seed outward to the desired diameter (2-c). The crystals continue to grow in length as long as the process conditions are

maintained. The applied temperatures and pressures, as well as the rotation and extraction speed, all have a direct effect on the diameter and the quality of the ingot. When the desired growth is reached, the seed and bonded ingot are removed from the chamber. The result is an ingot with all the physical

characteristics of the original seed material (2-d). See photo at left. Before moving to the next stage of production, a diamond saw is used to remove the cone and the remaining cylindrical ingot is ground and polished.

The Wafer

A diamond saw is used to slice the ingot into crystalline wafers or substrates that are less than 250 microns thick (10 mils). This is illustrated in Figure 3. After slicing, the wafer is subjected to a lapping and/or etching process in order to carefully remove unnecessary or damaged particles from the surface. Lapping is a physical process that involves moving the wafer over a plane of liquid abrasive, while etching is a chemical process intended to dissolve unwanted material. Both are used to ensure a smooth surface. Next, the thickness and flatness of each wafer is measured, and the wafers are sorted and polished in order to improve the efficiency and quality of downstream processing and make the wafers more receptive to additional layers of semi-conductive material.

Any imperfections created when the ingot is formed and sliced or when the wafer is lapped, etched or polished will lead to a poorly functioning or non-functioning LED. Unclean wafers also have a negative effect on the performance of the final diodes. As a result, all wafers are cleaned using

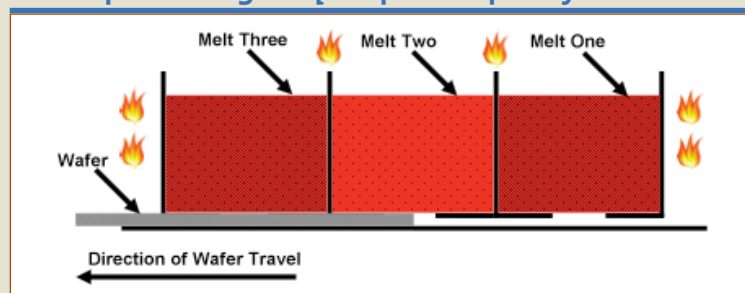
FIGURE 3

Wafers being sliced from ingot



FIGURE 4

Wafer processing—liquid phase epitaxy



ultrasonic or solvent-based methods in order to remove any remaining dirt, dust or foreign matter.

Next, a process known as Liquid Phase Epitaxy is used to grow additional layers of semiconductive material on top of each wafer. These layers often contain intentionally added impurities or dopants that improve the emissive characteristics and efficiencies of the final diodes. The dopants interfere with the crystalline structure of the die resulting in an altered output when a voltage is applied. All epitaxial layers have the same crystal orientation as the ingot; however, the existence of dopants means that each layer has a different electronic density.

Each epitaxial layer is several microns thick, and the process involves passing each wafer underneath various reservoirs of molten material or melt as illustrated in Figure 4. A melt can contain one or several types of dopants. If multiple dopants are needed to produce the desired effect, they can either be grown on the wafer structure in sequential layers or all at once.

Sometimes it is necessary to further increase the quantity of dopants or introduce new dopants into the wafer structure after the epitaxial layers are grown. This step is often administered using a continuous diffusion furnace

or furnace tube where dopants are forced into the upper layer(s) using high temperature gases. A photo of one such furnace is shown below.

The next step is to add conductive metal contacts or circuitry to the wafer. This may be done all at once or built up sequentially by repeating the following photoresist and vapor deposition process several times. First, a light-sensitive, liquid material called a “photoresist” is applied to the top surface of the wafer while it spins. Spinning ensures that the material is evenly distributed across the entire surface. Next, the wafer and applied resist are baked at a low temperature in order to harden the resist surface. A mask (also called a “reticule”)

containing the metallic contact pattern is placed over the wafer. The entire wafer is then exposed to UV light. All exposed areas of the resist material that are not blocked by the reticule cure underneath the light and are subsequently washed away in a developer bath. The resist that was under the mask remains on top of the semiconductor layers. It will be removed in a later step.

Contact metal is then evaporated onto the wafer in the areas where the resist was removed. This is done in a high-temperature, vacuum-sealed chamber flooded with a mixture of hydrogen and nitrogen gas. High temperatures are used to vaporize the metal contact material inside the chamber. Once the metal is vaporized, the chamber conditions are adjusted in order to condense the metal onto the wafer in the areas where the resist was removed. The remaining resist is then stripped in a chemical bath leaving just the epitaxial wafer and metal contacts. Finally, the contact pattern is annealed to the wafer in a high temperature furnace over a period of several hours. The end result is a chemical bond between the semiconductor and the contacts. An example of a processed wafer is provided in Figure 5.



Wafers pictured in front of furnace tube entrance.

FIGURE 5

Processed wafer



The Die (Chip, Diode, Semiconductor)

Depending on the diameter, a fully processed wafer is made up of thousands or even tens of thousands of individual LEDs all with the same general material structure and metallic contact pattern. Figure 6 shows one LED die resting on the face of a U.S. penny. This single die would have been one of many cut from a 2-, 4-, 6-, 8- or 12-inch diameter wafer using a laser or diamond saw.

After the dies are extracted from the wafer, a forward voltage is applied to each and every die, and the output is measured using an integrating sphere. It is only at this time that manufacturers know whether the

production process was successful. Each functioning LED is then binned according to wavelength, peak irradiance, and forward voltage. For additional information on integrating spheres and binning, refer to “UV-LED Overview Part I—Operation and Measurement.”

After the diodes are binned, they must be packaged according to the intended application. The semiconductor manufacturer will often package the dies itself before selling the LEDs to the market as modules. Alternatively, some semiconductor manufacturers will sell the individual dies without further packaging. In this case, the packaging is done directly by the final equipment manufacturer or other supplier. The packaging of UV-LEDs was detailed in “UV-LED Overview Part II: UV Curing Systems.”

Conclusion

The evolution of LEDs has spanned 187 years since the invention of Silicon Carbide; 118 years since the commercialization of Carborundum; 104 years since the discovery of electroluminescence; 83 years since the light relay was first conceptualized; 56 years since the initiative to engineer semiconductive man-made compounds;

19 years since the first UV-LED was produced in a lab; and eight years since UV-LED curing systems were first offered to the market. It has been a long and remarkable journey that has involved extensive development of previously unknown compounds; the creation of diverse diode structures; and the invention and optimization of precision manufacturing methods.

Despite all the amazing accomplishments, this is a journey that is still far from over. During the foreseeable future, UV-LED performance will continue to improve. More wavelengths will become available; higher irradiances will be generated; efficiencies will increase; lifetime hours will improve; and costs will become more attractive. These breakthroughs will not necessarily happen overnight, but recent advancements evaluated in the historical context of LED evolution make it hard not to be excited about the technology's future and all its possibilities. ▀

References

1. Schubert, E. Fred. *Light-Emitting Diodes*. Cambridge, UK: Cambridge University Press. 2008.
2. Held, Gilbert. *Introduction to Light Emitting Diode Technology and Applications*. Florida, USA: Auerbach Publications. 2009.
3. *Light-Emitting Diode*. How Products Are Made, Volume 1. 2006 - 2011. April 4, 2011. <http://www.madehow.com/Volume-1/Light-Emitting-Diode-LED.html>
4. *Silicon Wafer Processing*. IISME. Summer 2000. April 4, 2011. http://iisme.org/etp/Silicon_Wafer_Processing.pdf

—Jennifer Heathcote is general manager, North America for Integration Technology in Chicago, Ill.

FIGURE 6

Completed individual die shown in proportion to a U.S. penny

