Through a glass, darkly

The story of light-emitting diodes is one of creeping ever further up the frequency spectrum. With several big semiconductor firms now mass-producing light-emitting diodes in the ultraviolet range, these devices are set to replace mercury-vapour lamps in a range of applications. **Richard Corfield** reports

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Giving evidence Could ultraviolet LEDs change the future of forensic science?

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The humble light-emitting diode (LED) has come a long way since its origins in 1960s America. There, in the heady days of the semiconductor revolution, researchers at labs including RCA, General Electric, Bell and Texas Instruments worked to develop modern LEDs. The first of these could only emit infrared light, but doping the materials with additives soon led to LEDs that emitted visible light. Some of us still remember the resulting red-on-black displays on our Texas Instruments calculators and Casio watches.

Since then, the light-emitting capabilities of LEDs have crawled inexorably up the frequency spectrum, through the visible range and entering most recently the ultraviolet (UV) realm with wavelengths shorter than 400 nm. Work began on developing UV LEDs in the late 1990s and within a few years the first products became commercially available, with the wavelength being driven down ever since from near-ultraviolet (NUV) (approximately 300–400 nm) into deep-ultraviolet (DUV) (approximately 200–300 nm).

In the past few years, DUV LEDs have finally become commercially available cheaply and in large quantities. As a result, firms have begun to harness their huge potential to revamp applications that currently rely on mercury-vapour UV lamps, such as corrective eye surgery and forensic analysis. What is more, now that researchers understand how to make high-quality DUV LEDs, only a few more steps are needed to make laser diodes. These devices would enable techniques that were not possible before, such as optical storage in the UV range and a more practical form of anthrax detection.

Conquering the technology

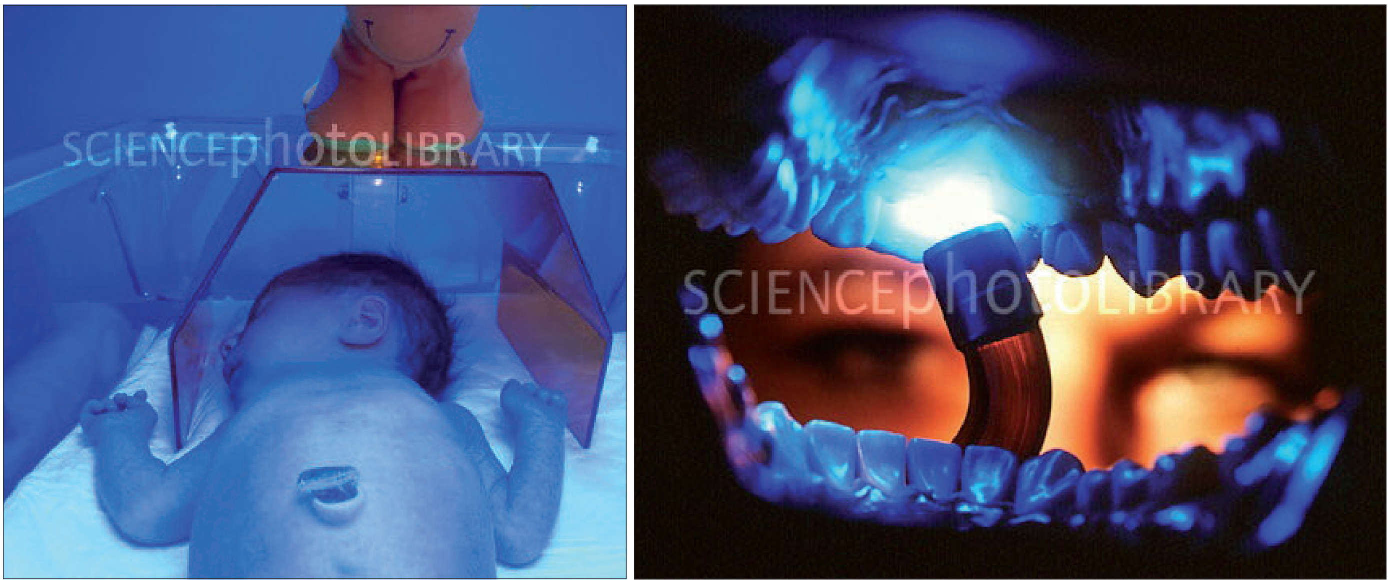
The Japanese company Nitride Semiconductors developed the world's first UV LED in 2000, but other companies in Japan and elsewhere are also now getting in on the act. The market for these devices grew from $20m in 2008 to $90m in 2014. Yoshihiko Muramoto, Nitride's president and chief executive officer, told *Physics World* that the exponential growth in the applications for UV LEDs has largely been led by improvements in crystal growth, chip-processing and packaging technologies. As a result, says Muramoto, UV LEDs have come far in the past decade. Their efficiencies have now reached 60% at a wavelength of 405 nm, 50% at 385 nm and 30% at 365 nm. In addition, the latest models emit light with a power of up to 12 W, which is a hundred-fold increase on what was possible 10 years ago. At the same time, costs have fallen as a result of mass production, making them more affordable.

The scientific journey to reach this point has not been easy, even though a UV LED works on the same principles as any other LED. At its most basic, a voltage applied across a p–n junction diode causes light to be emitted as electrons recombine with electron holes, with the electronic energy levels – and hence the energy of emitted photons – depending on the material and doping choices. (For more on the physics of LEDs, see box on pXX.) The wavelength of a gallium–nitride LED is controlled by adding the dopants indium and aluminium in different ratios. More indium results in a shift to longer wavelengths, and more aluminium results in a shift to shorter wavelengths. So, while a conventional blue LED is made primarily of indium–gallium–nitride, a DUV LED is made primarily of aluminium–gallium–nitride.

Increasing the aluminium-to-indium doping ratio to achieve shorter wavelengths, however, has the downside of decreasing efficiency. As Muramoto explains, making the emission wavelengths of the LED shorter than 400 nm means having to dope aluminium in the active layer of the p–n junction. "But free electrons of aluminium are difficult to release because of their strong attraction to the atomic nucleus, so we need high temperatures of around 1200 °C to grow the UV LED wafer," he adds.

The problem is that these temperatures cause a problem for the dopant layer. "It is very hard to control the flow of gas accurately and achieve a uniform layer of the dopant on the sapphire substrate," says Muramoto. To get around this problem for DUV LED wafers, a buffer layer of aluminium–nitride is first deposited on the sapphire substrate.

So complicated is the physics behind the manufacture of DUV LEDs that Japanese manufacturer Nikkiso, which has been developing these devices since 2006, enlisted the help of Isamu Akasaki of Meijo University and Hiroshi Amano of Nagoya



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Multipurpose Ultraviolet light has a wide range of uses, including treating jaundice in babies (left) and hardening the resin of tooth fillings (right).

University, who went on to share the 2014 Nobel Prize for Physics for their work on blue LEDs with Shuji Nakamura of the University of California, Santa Barbara. Under their guidance, the firm modified its mass-production technologies and began selling samples of DUV LEDs in 2012.

According to Yole Développement, a technology consultancy based in Lyon, France, UV LEDs will be the next major step forward in LED technology. Pars Mukish, a consultant with the company, points out that a lot of this potential is due to recent international agreements that limit the production, use and trade of mercury. These include the Minamata Convention on Mercury, which so far has 128 signatories including Japan, China and the US. As a result, the production of mercury-vapour lamps, which currently dominate the market for UV-light applications, is set to decline, leaving a large gap in the market that only UV LEDs can fill.

Out with the old

Mercury-vapour lamps are used in many technologies, and it is not only international agreements that make their replacement with UV LEDs inevitable. The simple fact is that UV LEDs have many advantages over mercury lamps: they are more efficient, last longer and emit light at a more constant intensity. It is also easy to control their temperature and heat.

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As well as the NUV/DUV differentiation, the UV range has traditionally been divided into the three categories UV-A, UV-B and UV-C. Applications in the UV-A range (315–400 nm) include identifying counterfeit currency and curing resin, which involves the cross-polymerization of a UV-photosensitive material such as an ink, adhesive or coating. Dentists, for example, use UV lamps to rapidly harden the UV-sensitive resin of tooth fillings. The intensities of 1–10 W cm^{-2} required for some types of resin curing have already been reached by LEDs in the NUV range, but power isn't everything. Another factor to consider is the emission spectrum of the light source being used. UV LEDs have a much narrower spectrum than mercury-vapour lamps, and it has been found that, for example, a 365 nm UV LED did not provide the precise wavelength needed to initiate curing.

Shorter UV-B wavelengths (280–315 nm) are used in phototherapy, for example to treat jaundiced babies to oxidize the liver pigment bilirubin. In the original version of this therapy, the baby is laid under a mercury-vapour lamp with its eyes protected by goggles, far enough from the lamp so as not to overheat. An improvement to this technique, allowing parent and baby to stay together, was to feed the light through optical fibres to a blanket wrapped around the baby. Less cumbersome still will be a version that simply incorporates UV LEDs into the blanket itself.

In adults, meanwhile, UV phototherapy helps in the treatment of psoriasis and other skin conditions. Psoriasis is a persistent and chronic skin disease that tends to be genetically inherited. The effects of psoriasis can range from a small, localized area to the entire body. With conventional mercury-vapour lamps, improvement can be seen in as little as three weeks, with maintenance therapy thereafter. LEDs will deliver the same benefits in a more convenient and efficient way.

UV light sources are also fundamental tools for forensic investigation. At crime scenes, fluorescein (a common fluorescent dye) is sprayed onto surfaces to reveal human DNA evidence such as blood, semen, skin oils and amino acids, the fundamental building blocks of proteins. UV illumination is also used by the police to discover former wounds, bite marks and bruises for six to nine months after the injury was inflicted – the kind of evidence that could prove pivotal in a court case. UV-LED-based devices will be more portable and powerful than current alternatives.

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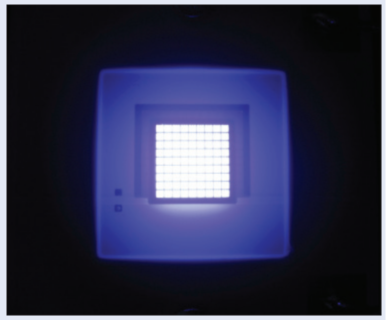
The old way Mercury-vapour lamps are the current standard UV light source, but they have many disadvantages that LEDs do not have.

The shortest wavelengths of UV are in the UV-C range (100–280 nm). This type of UV can sterilize water, air and surfaces by breaking up the nucleic acids – including DNA and RNA – of micro-organisms, so preventing them from reproducing. Nucleic acids readily absorb UV radiation, especially in the 240–290 nm range. The UV absorption in DNA peaks at around 260 nm, which is the range that has just been accessed by advancements in DUV LEDs. As LEDs take over from mercury lamps, costs will come down and efficiencies soar, not least because the LEDs will be cooled as the water being sterilized passes over them. The city of New York has recently installed a UV-based sterilization system based on mercury-vapour lamps and it is likely that in the future other cities will install such systems based instead on LEDs.

Beyond mercury

Replacing mercury lamps with LEDs has many benefits, but it does not enable any applications that were not possible before. A UV laser diode (LD), on the other hand, would open up some entirely new possibilities, especially in tandem with a photodiode (light detector) at the same wavelength. And as has been seen at longer wavelengths, once the manufacture of high-quality LEDs at a certain wavelength is understood, LDs at the same wavelength follow soon after. UV lasers do already exist, but they are impractical for many applications as they are over a cubic metre in size, they create lots of heat – requiring cooling systems – and they are expensive. LDs would combat all of these problems – in particular the size and heat – and so there is considerable motivation to create them.

How LEDs work



Nitride Semiconductors

The new way An ultraviolet LED made by Yoshihiko Muramoto and colleagues.

In a light-emitting diode (LED), electrical energy is converted into light energy in the form of photons that are emitted from the device. Typically they emit a narrow bandwidth of wavelengths from infrared to ultraviolet. They can also be constructed to emit laser light.

To make an LED, an electron-rich semiconductor and an electron-poor semiconductor are joined to form a p–n junction. This is a junction between two types of semiconductor material that have different proportions of electrons to electron-accepting holes. Applying a voltage across this junction causes electrons to move energy levels and produce photons – for example when electrons "fall" into empty holes in the p-layer of the p–n junction. This happens in any diode – for example, in a standard silicon diode; however, in this case the frequencies of the emitted photons are so low that they are in the infrared part of the spectrum and invisible to the human eye.

This explains why doping the p–n junction is crucial to the frequency of light that is produced. Normal diodes, which are used for detection or power rectification, are made from either germanium or silicon. LEDs, in contrast, are made from exotic semiconductor compounds such as gallium–arsenide (GaAs), gallium–phosphide (GaP), silicon–carbide (SiC) or gallium–indium–nitride (GaInN), all mixed together at different ratios to produce light with a distinct wavelength.

One use of UV LDs would be the next generation of optical storage. From CDs, through DVDs and most recently to Blu-ray discs, lasers at ever shorter wavelengths (780 nm, 650 nm and 405 nm, respectively) have been coupled with discs with increasingly microscopic indentations in order to boost data-storage capacity. DUV LDs and photodiodes could be used in future to enable the next jump to higher storage capacity.

UV LDs in the short-wavelength range could also be used in security scanners. In the weeks following the terrorist attacks of 9/11, several letters laced with anthrax appeared in the US mail. Five Americans were killed and 17 became ill in what became the worst biological attacks in US history. As a preventative measure, mail now has to be scanned using an "electronic nose" device connected to a DNA sequencer. But Anthrax contains the organic compound tryptophan, which has a peak absorbance of about 280 nm. If a laser tuned to this frequency is aimed at a sample containing tryptophan, the tryptophan fluoresces with emitted radiation at a longer wavelength, which can be easily monitored. Current detectors based on this technique use excimer lasers, which are bulky and expensive; UV LDs could help roll out the technology more widely.

In short, any application that currently uses mercury-vapour lamps will soon be replaced by UV LEDs. The frequency problem has been solved and now the dark light of ultraviolet is ready to be deployed more safely and efficiently than ever before. ■