Going deep for UV sterilization LEDs

Researchers and leading nitride semiconductor device firms are looking to shorten the wavelength of commercial light-emitting diodes to ~250nm. Mike Cooke reports on progress and possible applications.

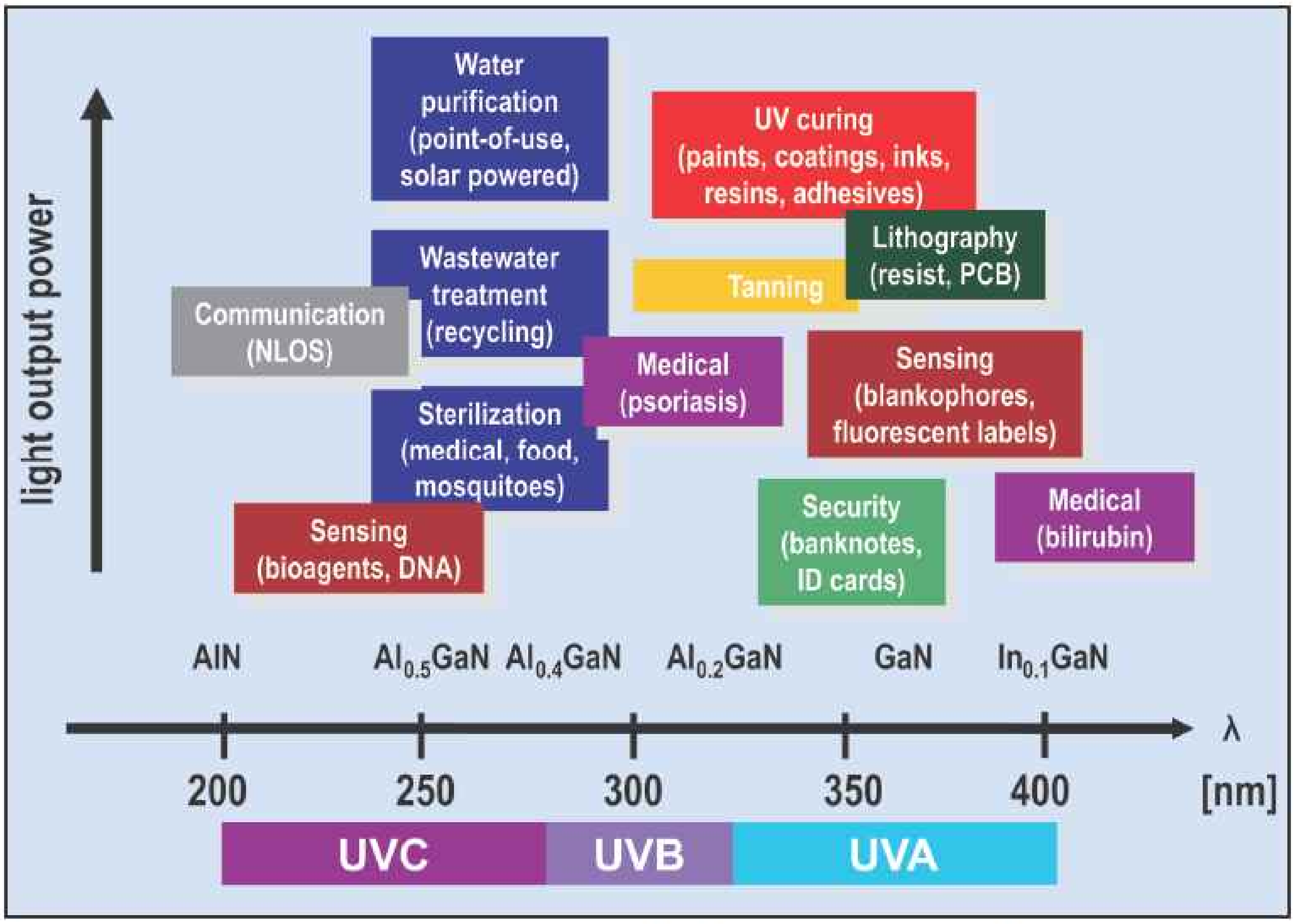

Figure 1. Potential applications for UV LEDs. Image from [1].

Ultraviolet (UV) light has a wide range of actual and potential applications (Figure 1). Although LEDs and laser diodes have been commercially developed in the near-UV region (less than 400nm), as the wavelength shortens construction of such devices become much more challenging.

Current drivers of 'deep UV' LED development (DUV, loosely shorter than 350nm wavelength, more strictly less than 300nm) is for water treatment and sterilization of medical equipment. UV sterilization/purification systems need to produce photons with wavelengths shorter than about ~260nm, giving them the energy needed to break chemical bonds between corresponding base pairs within deoxyribonucleic acid (DNA) and ribonucleic acid (RNA) polymers of micro-organisms such as bacteria and viruses. Rather than forming the usual hydrogen-bonded thymine-adenine (T-A) base pairs in the DNA double-helix, neighboring thymine pairs on a single chain form covalent bonds, disrupting the genetic code (Figure 2). UV sterilization can therefore be effective against bacteria that are resistant to normal thermal treatments.

The traditional competitor for such applications is radiation from the 254nm emission line of mercury lamps. Particular attractions of LEDs are their compactness and more environment-friendly character when compared with breakable, highly toxic mercury lamps. Further advantages of LEDs when fully developed should include lower energy consumption, better robustness and longer operation time before failure.

The US and Japan governments have funded a wide range of research towards shorter-wavelength UV LEDs under such bodies as Japan's National Institute of

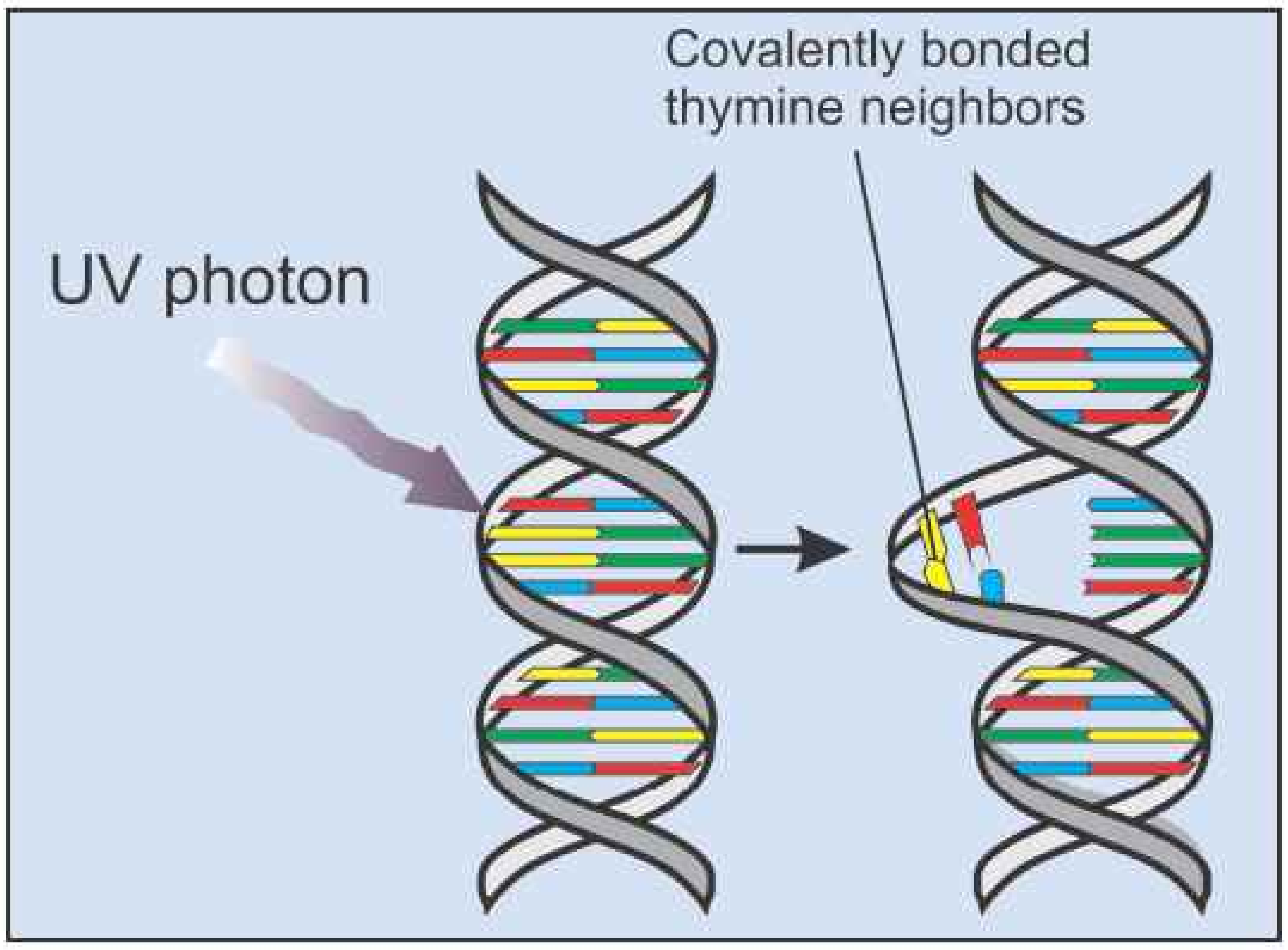

Figure 2. Effect of UV radiation in disrupting thymine-adenine (TA) bonds and creating covalently bonded thymine neighbors. Based on NASA source.

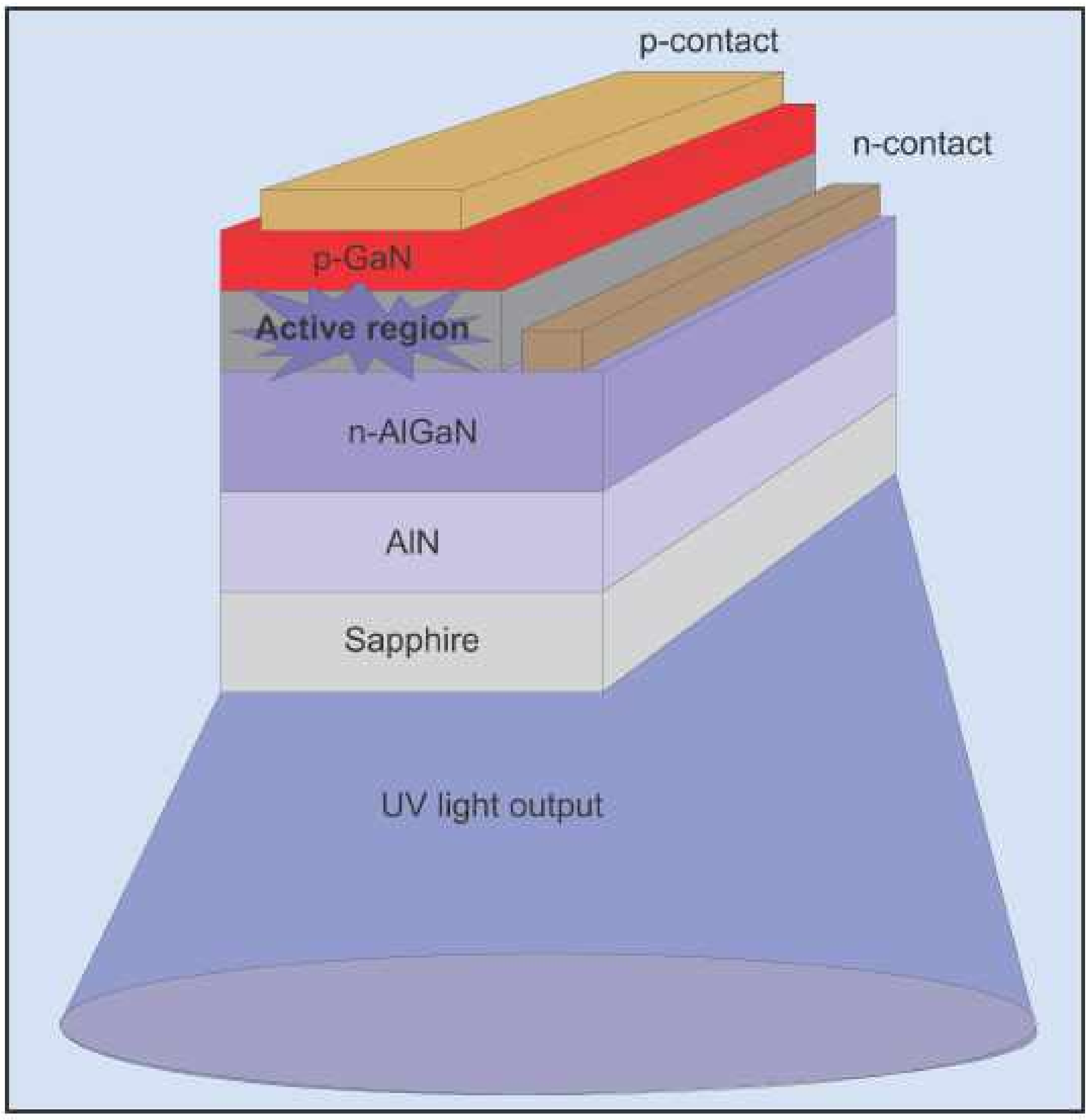

Figure 3. Simple nitride semiconductor UV LED.

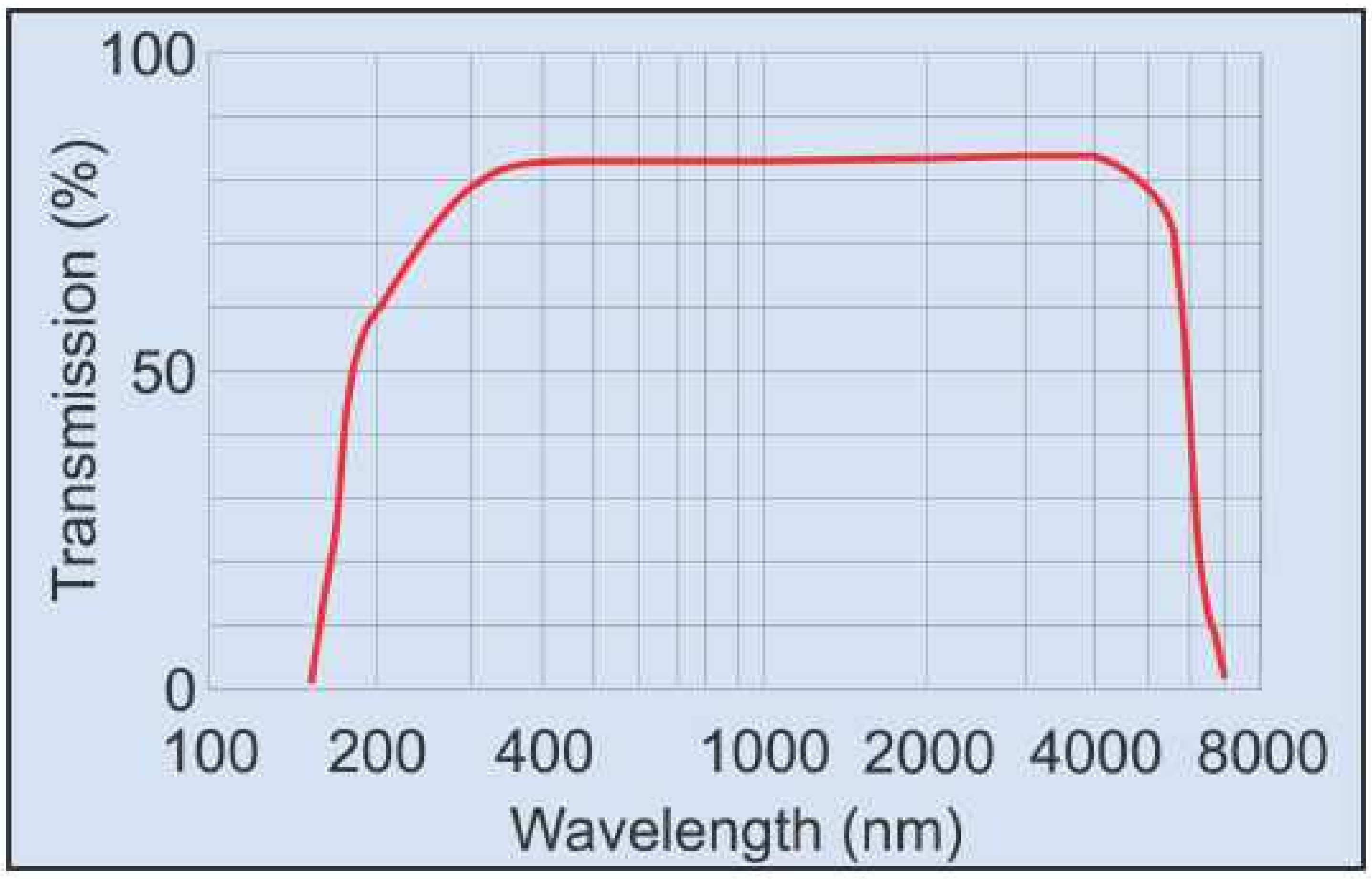

Figure 4. Typical transmission curve for sapphire.

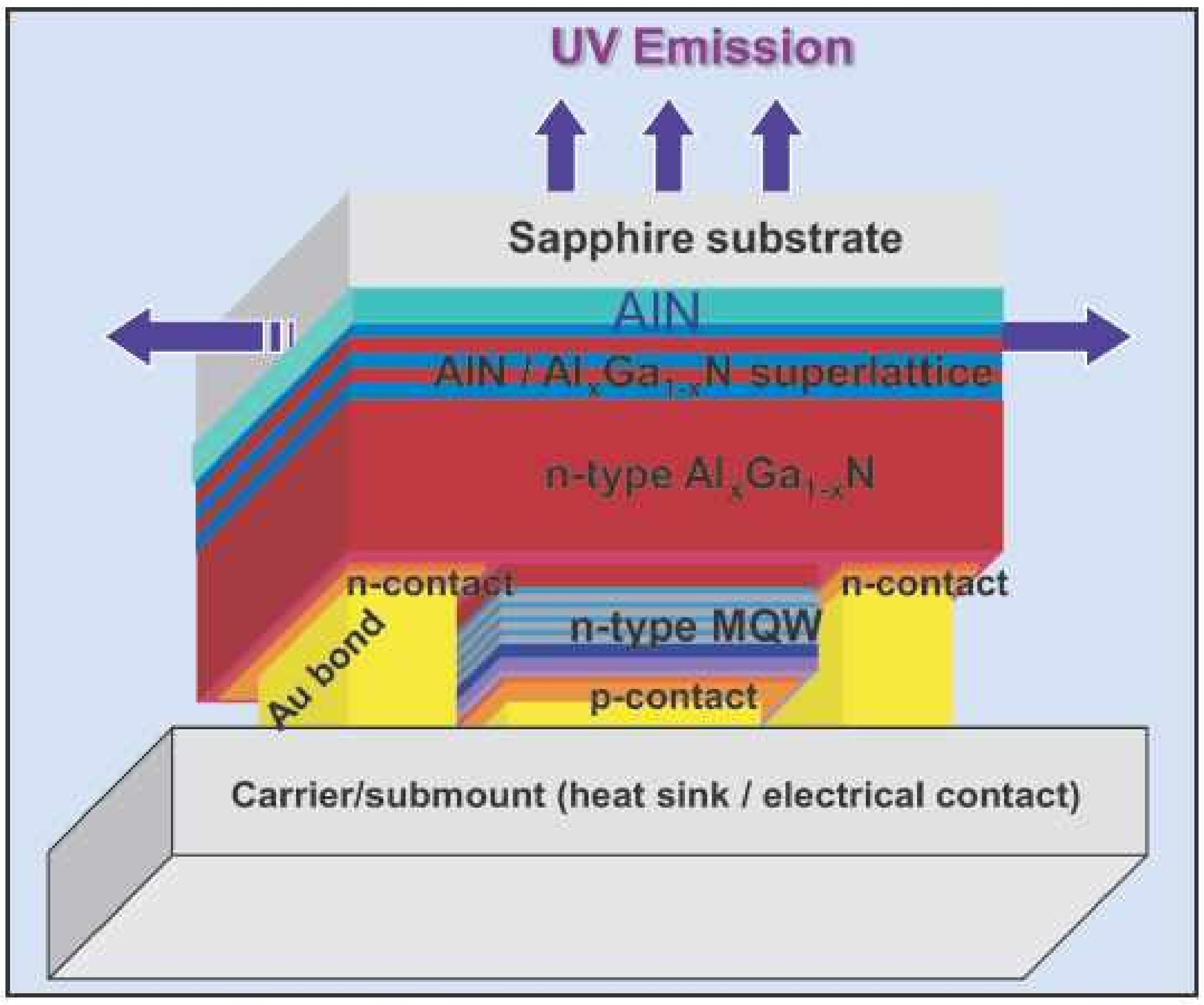

Figure 5. Schematic of flipped UV LED. Image from [2].

Advanced Industrial Science and Technology (AIST) and the US Defense Advanced Research Projects Agency (DARPA). The latter organization set up a Semiconductor Ultraviolet Optical Sources (SUVOS) program in 2002. This year DARPA launched a new effort aimed at Compact Mid-Ultraviolet Technology (DARPA-BAA-10-45@darpa.mil) looking for efficient 'mid-ultraviolet' (200–300nm) emitters. The project is to develop heteroepitaxy, waveguides, cavities and contacts to enable efficient LEDs and chip-scale semiconductor lasers operating at wavelengths below 275nm. It is hoped the resulting devices will achieve small, low-weight, high-output power/efficiency for chemical/biological-agent detectors and portable water purification illuminators.

Structure

Most UV diodes are based on aluminum gallium nitride (AlGaN) alloys in a p–n format (Figure 3). The nitrides are deposited on sapphire substrates that are relatively transparent to UV radiation (down to ~250nm wavelengths, see Figure 4). Silicon is generally used as n-type dopant; magnesium is the p-type acceptor impurity.

The active, UV-emitting region is usually not intentionally doped and may consist of single or multiple wells of narrower bandgap material separated by barriers. Since sapphire is non-conducting, the electrical contacts are made from the "top" of the device, with the p-contact made by depositing suitable material to the p-type layers. The n-contact requires etching through the p-contact and active layers before depositing contact metal alloy. The resulting UV die is flipped onto a submount and packaged with the UV-transparent sapphire substrate uppermost to allow emission from the device (Figure 5).

►

Table 1. Recent achievements for DUV LEDs. (* @150mA).

[Reference]	Wavelength nm	Output mW	Current mA	Voltage V	EQE %
Saitama [3]	240	1.2	240		0.13
SET [4]	245				0.18*
SET [2]	247	6	300		
SET [4]	247	2	225		0.15*
Saitama [5]	250	4.8	135		1.18
Saitama [6]	258	0.2	10		0.3
Saitama [5]	262	10.4	165		1.54
SET [3]	273	30	700	6.5	
Nichia [7]	281	2.45	20	7.53	2.78
USC [8]	307	20	20		
Dowa [9]	320–350	1.4	20		

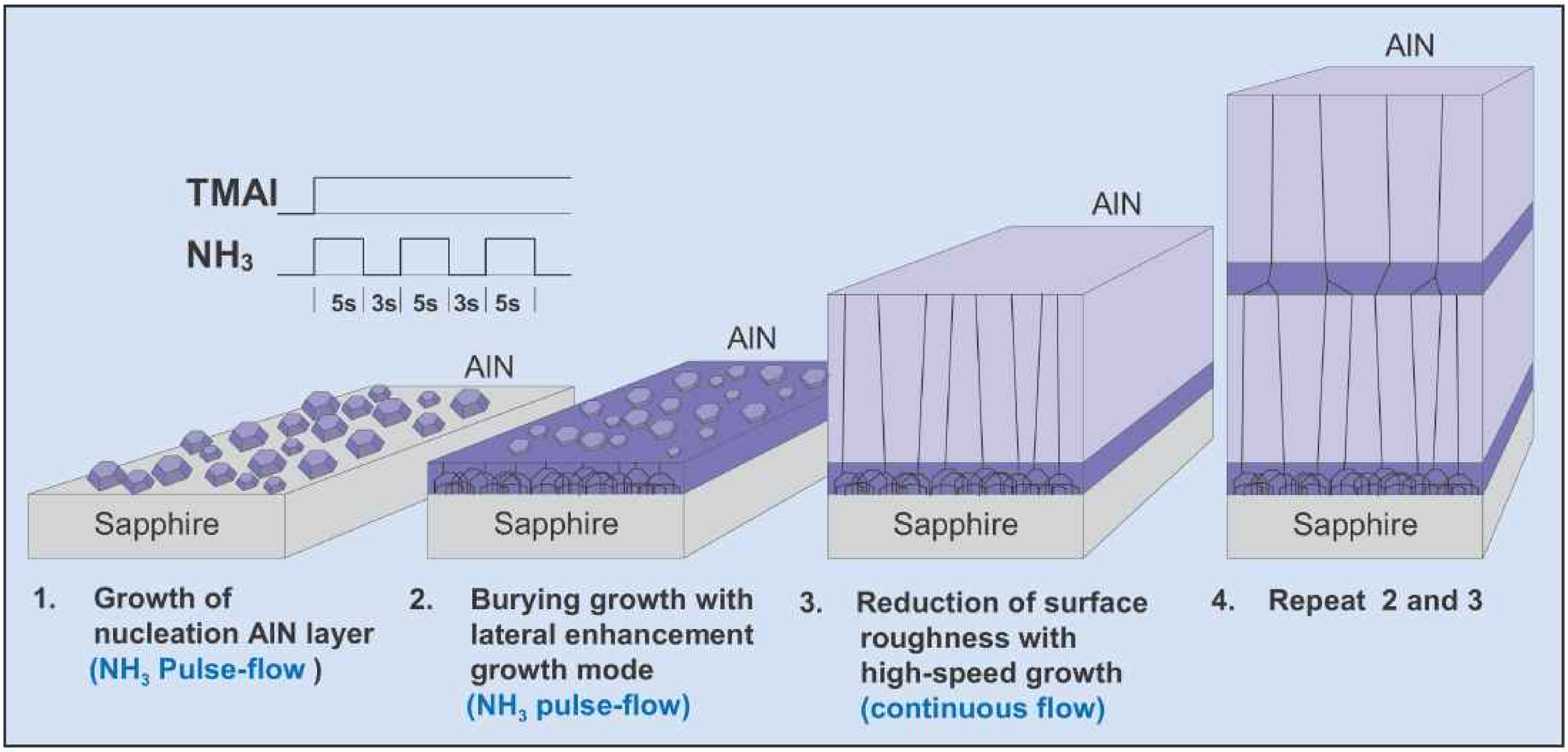

Figure 6. Gas flow sequence and schematic of the growth control used for NH$_3$ pulse-flow multilayer (ML)-AlN growth technique that aims to reduce threading dislocations and result in crack-free substrates.

To make practical UV LEDs, many features have to be added to these simple concepts to improve the crystal and electrical structure of the materials. These include buffer layers to bridge the lattice mismatch between the sapphire substrate and the AlGaN material system and electron-blocking layers (EBLs) to maximize the recombination in the active region rather than in the p-contact where non-radiative and unwanted longer-wavelength recombination occurs. Other features such as thermal management, increasing light extraction and improving the performance of the p-contact for hole injection are also vital to improving performance.

Researchers are working hard (Table 1) to bring the relatively low external quantum efficiencies (EQEs) of DUV LEDs (usually less than 2%) nearer to the achievements of visible LEDs (up to 70%).

Substrates/templates

The base 'template' for nitride-based UV LEDs is usually an AlN layer deposited on sapphire wafers. Although aluminum nitride (AlN) crystal substrates are also possible contenders for UV application, such substrates have yet to be successfully developed.

Table 2. Structure of wells and barriers (x is Al molar fraction) and maximum output power under cw operation for recent LEDs produced in Saitama [3].

Wavelength nm	AlGaN well x	AlGaN barrier x	Max. power mW
234	0.74	0.84	0.4
240	0.68	0.8	1.2
254	0.61	0.76	4
264	0.53	0.7	11.6

As is often the case with nitride semiconductors, dislocations from the template that thread through subsequent epitaxial structures are often blamed for the low EQEs. A number of techniques have been developed to reduce the density of these threading dislocations.

Some of these techniques can be quite elaborate, such as epitaxial layer overgrowth (ELOG), where masks are used to restrict the seeding areas for crystal growth. By restricting the number of crystal orientations in the overgrown material, one can significantly reduce the threading dislocations to where the different orientations meet.

From a commercial perspective, simpler is better. Hence, many researchers are seeking improvements in crystal quality that can be directly implemented in the growth chamber, rather than having to use mask and etch.

Sensor Electronic Technology (SET) has patented a proprietary migration-enhanced metal-organic chemical vapor deposition (MEMOCVD) that, combined with conventional MOCVD, it uses to produce its nitride devices. The MEMOCVD technique is based on controlling the duration and waveform of the precursor pulses. The pulses of different precursors may even overlap. This allows the growth temperature to be reduced, giving improved atomic incorporation, surface coverage and thickness uniformity. MEMOCVD has been shown to improve AlGaN material quality up to 0.75 Al molar fraction.

Researchers based in the city of Saitama in Japan have used low-pressure metal-organic

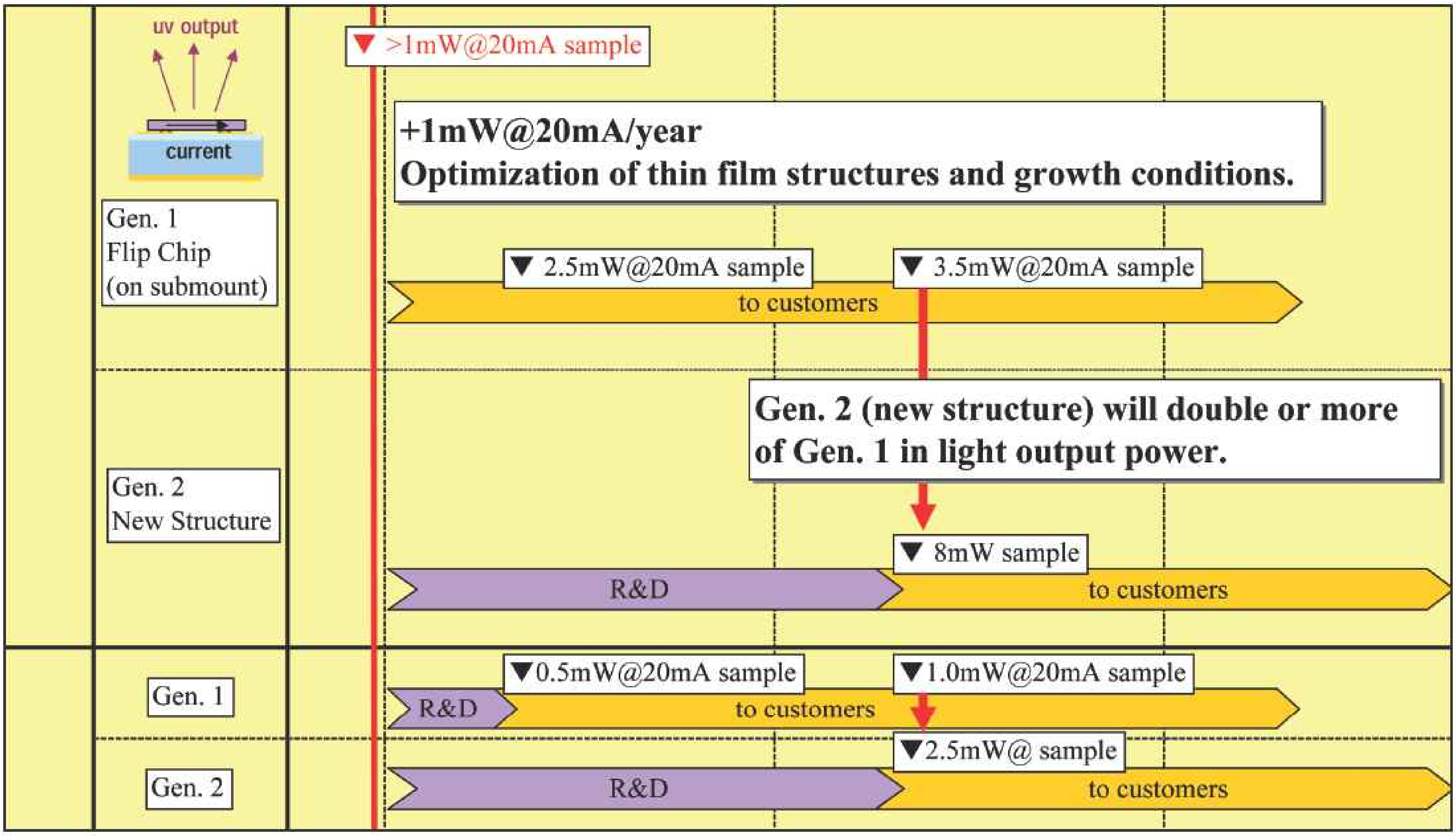

Figure 7. Dowa roadmap (2010–2012) for developing and commercializing shorter-wavelength UV LEDs.

chemical vapor deposition (LP-MOCVD) to grow their DUV LEDs on aluminum nitride (AlN) on (0001) sapphire templates. These AlN buffer layers are grown using a pulsed-flow multi-layer (ML) method using ammonia as the nitrogen source (Figure 6). By alternating pulse and continuous flow growth one can obtain crack-free, thick AlN layers with an atomically flat surface with a stable Al (+c) polarity. The method depends on enhanced precursor migration during the pulse sequence. Edge-type dislocation densities of less than 7x10^8/cm^2, as estimated through XRC of 350–370arcsec for the $(10\bar{1}2)$ plane, have been achieved. These researchers are affiliated variously with Institute of Physical and Chemical Research (RIKEN), Saitama University and Japan Science and Technology Agency (JSTA) Core Research of Evolutional Science & Technology (CREST) basic research promotion program.

Last year, these researchers reported progress in using ML templates to improve performance for DUV multi-quantum well (MQW) LEDs (Table 2) with wavelengths as short as 234nm [3]. "High output power" was achieved for 240nm DUV LEDs. Working with Panasonic Electric Works, the team has even achieved wavelengths of 222nm [10]. Panasonic has no AlGaN growth techniques, but it does have large markets with potential for UV LED application, making it a useful partner with a view to making commercial UV LEDs.

The Saitama group has also used AlN/sapphire templates from Dowa Electronics with a 250–350arcsec FWHM (XRC) for $(10\bar{1}2)$ ω scans, resulting in devices emitting more than 1mW output power in the range 241–282nm. In particular, a 241nm device emitted 1.1mW, while a 256nm LED had a 4.0mW output (both CW at RT).

The ML-AlN process is still developing. RIKEN's Hideki Hirayama comments: "Our ML-AlN has recently achieved XRC$(10\bar{1}2)$ of 280–300arcsec and the uniformity is good across the 2-inch wafer (50mm). We believe the quality level is the same between our ML-AlN and Dowa's AlN. Actually, the EQE of 230–250nm UV LEDs show almost the same value when fabricated using Dowa's AlN as with RIKEN's ML-AlN." In addition to marketing 50mm diameter templates with an insulating 1μm AlN layer on sapphire, Dowa has recently produced its own prototype LED samples emitting in the longer wavelength range 320–350nm with 1.4mW output power at 20mA current and is seeking to start mass production. Technically, the company also hopes to increase the output power and shorten the wavelength (Figure 7), expecting a market worth 'tens of billions of yen' to emerge. The nitride semiconductor epitaxial layers are grown using technology developed by Xerox' Palo Alto Research Center (PARC) in the USA and RIKEN.

Japan's Nichia Corp has been using thicker AlN buffer layers to improve crystal quality using low-pressure metal-organic chemical vapor deposition (LP-MOCVD) with simultaneous trimethyl-metal and ammonia (NH_3) sources [7]. The deposition did not use any special techniques such as migration enhancement or pulsing. ➤

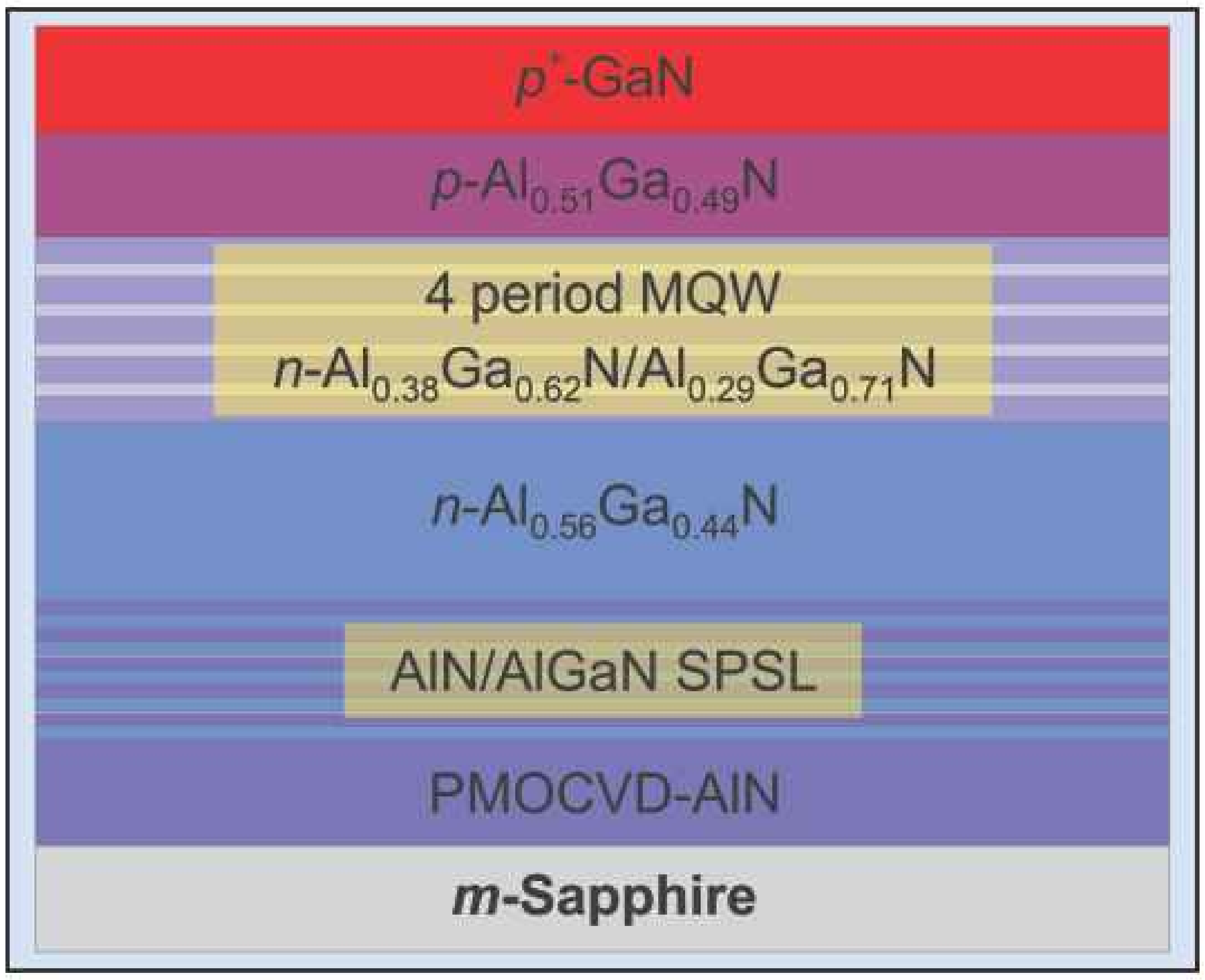

Figure 8. Schematic cross-section of USC/Nitek semipolar deep-UV LED structure.

The thickness of the base AlN layer was 3μm and x-ray diffraction analysis gave rocking curve (XRC) full-width at half maximum (FWHM) values of 60arcsec and 600arcsec for the (0002) and $(10\bar{1}2)$ crystal planes. The typical $(10\bar{1}2)$ FWHM for 1μm AlN layers is more than 1000arcsec. After the AlN template, an AlN/AlGaN superlattice was used to relieve strain arising from lattice mismatches before depositing the silicon-doped n-type contact layers.

Non-standard crystal orientation devices have also been developed. By starting with sapphire oriented in a different direction from the standard c-plane, it is hoped to reduce polarization effects that can lower recombination efficiencies by pulling electrons and holes apart. The first researchers to explore this possibility are based in South Carolina and have developed 'first demonstration' semipolar nitride semiconductor 307nm ultraviolet LEDs [8]. The 307nm wavelength is claimed as the shortest emission wavelength ever reported for a non c-plane III–nitride semiconductor based LED.

In nitride semiconductors grown in the normal 'c-direction', electric fields of the order of several MV/cm can build up due to polarization effects. Compared with longer wavelength indium gallium nitride LEDs (e.g. blue–green), it has been harder to develop such materials for UV wavelengths shorter than 350nm since the wide bandgap aluminum-based nitrides needed tend to form stacking faults and multiple structural phases when grown in non-standard directions.

The research by University of South Carolina and Nitek Inc used m-plane sapphire substrates (Figure 8). A layer of aluminum nitride is then grown using pulsed metal-organic chemical vapor deposition (PMOCVD). A strain-relieving short-period super-lattice (SPSL) of alternating ultra-thin layers of AlN and AlGaN is used to enable crack-free metal-organic chemical vapor deposition (MOCVD) of subsequent layers.

The x-ray diffraction measurements showed that the nitride layers grew in the $(11\bar{2}2)$ semipolar direction and that the SPSL was effective in improving the crystallinity of the material above — a typical rocking curve scan of a diffraction peak gave a full-width at half maximum (FWHM) value of 1386arcsec for the AlN template, but for the n-AlGaN contact layer this was reduced to a sharper ~1110arcsec.

The output power for the produced LEDs at 20mA DC input was 20μW, which the researchers find 'reasonable for the first ever demonstration of a semipolar deep-UV LED'. Further work is being carried out to improve the device design and material quality in the hope of increasing optical output powers.

Some companies that produce AlN ceramic materials have also developed AlN/sapphire templates. Dowa is one example. NGK Insulators is another that has devel-

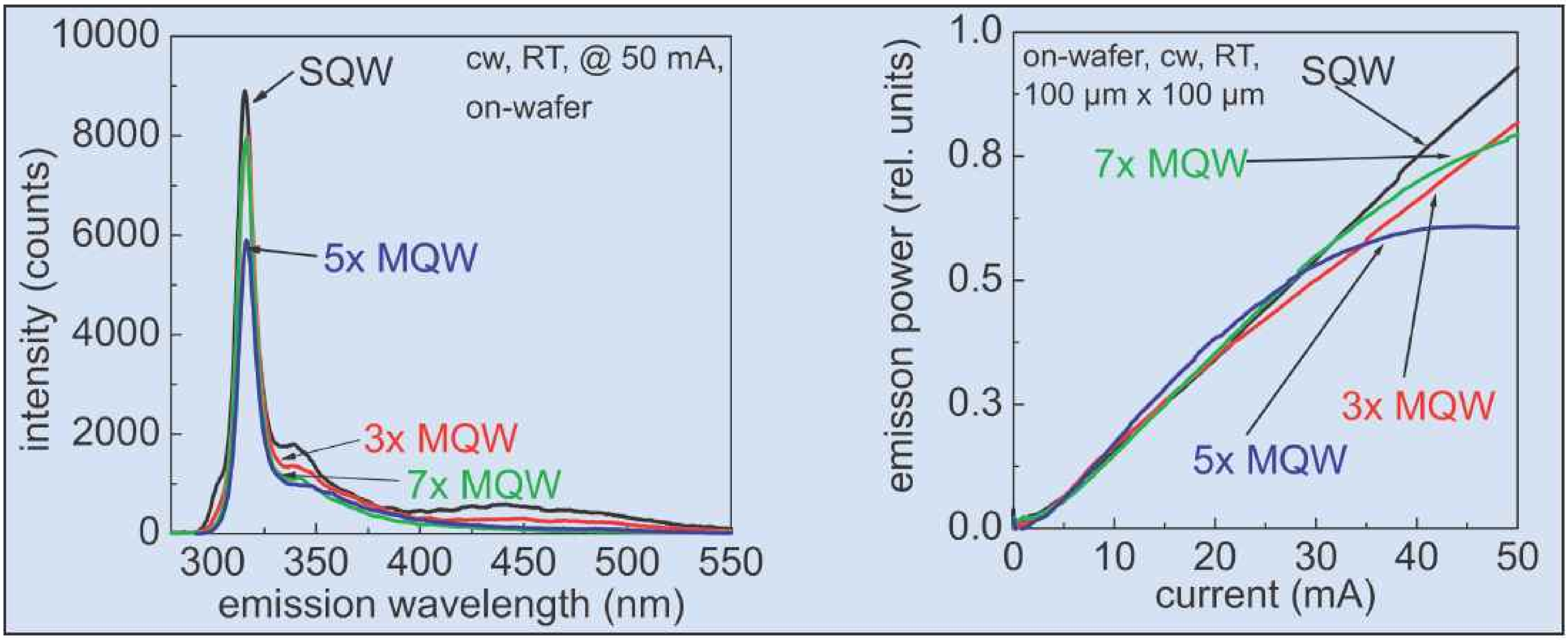

Figure 9. Variations of intensity/output power vs wavelength & current for different numbers of quantum wells.

oped, with Mie University in Japan, a self-produced low-pressure MOCVD system to deposit layers of AlN up to a micron thick on silicon carbide and sapphire [11]. The growth temperature for AlN on sapphire reaches around 1000ºC, higher than that for the subsequent epi-layers. XRC FWHM values of 40arcsec and 200arcsec have been achieved for (0002) and ($10\bar{1}2$) crystal planes, respectively, for 1μm-thick AlN layers.

Table 3. Al composition x of $Al_xGa_{1-x}N$ wells, buffer and barrier layers and multi-quantum barrier (MQB), along with maximum external quantum efficiency (EQE) and output power for LEDs with MQB.

Wavelength nm	Well x	Barrier/buffer x	MQB x	Max. EQE %	Max. power mW
250	0.62	0.77	0.95	1.18	4.8
262	0.55	0.72	0.94	1.54	10.4

Epi-layers

Having made or bought in the AlN/sapphire template, researchers/developers/producers generally turn to or continue traditional MOCVD deposition for the subsequent epi-layers. Technische Universität Berlin and Ferdinand-Braun-Institut für Höchstfrequenztechnik have been looking at different ways to optimize indium-doped AlGaN heterostructures for UV emission [1]. Among the variations explored in ~320nm devices, the group has looked at the use of AlGaN interlayers between the active region and the EBL, and variations on the MQW active region.

The effect of an AlGaN interlayer is to increase the MQW emission and suppress longer wavelength parasitic emissions in the p-type contact region. The MQW was varied both in number of wells (1 to 7) and in layer thicknesses. Increasing the number of wells reduced secondary peaks in the spectrum, but had little effect on the luminescence for continuous wave (cw)/DC currents up to 30mA (Figure 9). The thickness of the QWs had a greater effect, with the maximum output coming from 2.2nm wells.

The Saitama group of institutions has also tried indium-doping of the AlGaN quantum-well layers [6]. These devices use indium segregation effects, which are thought to enhance emissions through carrier localization in InGaN UV/blue LEDs.

Electron blocking and p-GaN contacts

Electron-blocking layers (EBLs) usually consist of a thin layer of semiconductor material with an energy bandgap wider than the other materials in the LED structure. The aim is to create a barrier to electrons, while maintaining a low barrier for holes to enter the active region of the device. At very short emission wavelengths, where large energy bandgaps are already being used in the active region, the relative effectiveness of single-layer EBLs is reduced.

A 2.7x efficiency enhancement from using multi-quantum barrier (MQB) electron-blocking layers is claimed for deep-ultraviolet (DUV) nitride semiconductor LEDs developed by the Saitama group [5]. The wavelengths of the devices were in the range 262–250nm, with some of the maximum output powers and EQEs described by the researchers as 'the highest values ever reported' (Table 3).

Multi-quantum barriers use interference effects from the wave-like behavior of electrons to enhance the barrier. The theoretical proposal for MQBs dates back to 1986 and the idea was applied in the early 1990s to aluminum gallium indium phosphide (GaInP/AlInP) red laser diodes (LDs). AlGaN devices were produced with single and multi-layer EBLs to show the effect of using MQBs (Figure 10).

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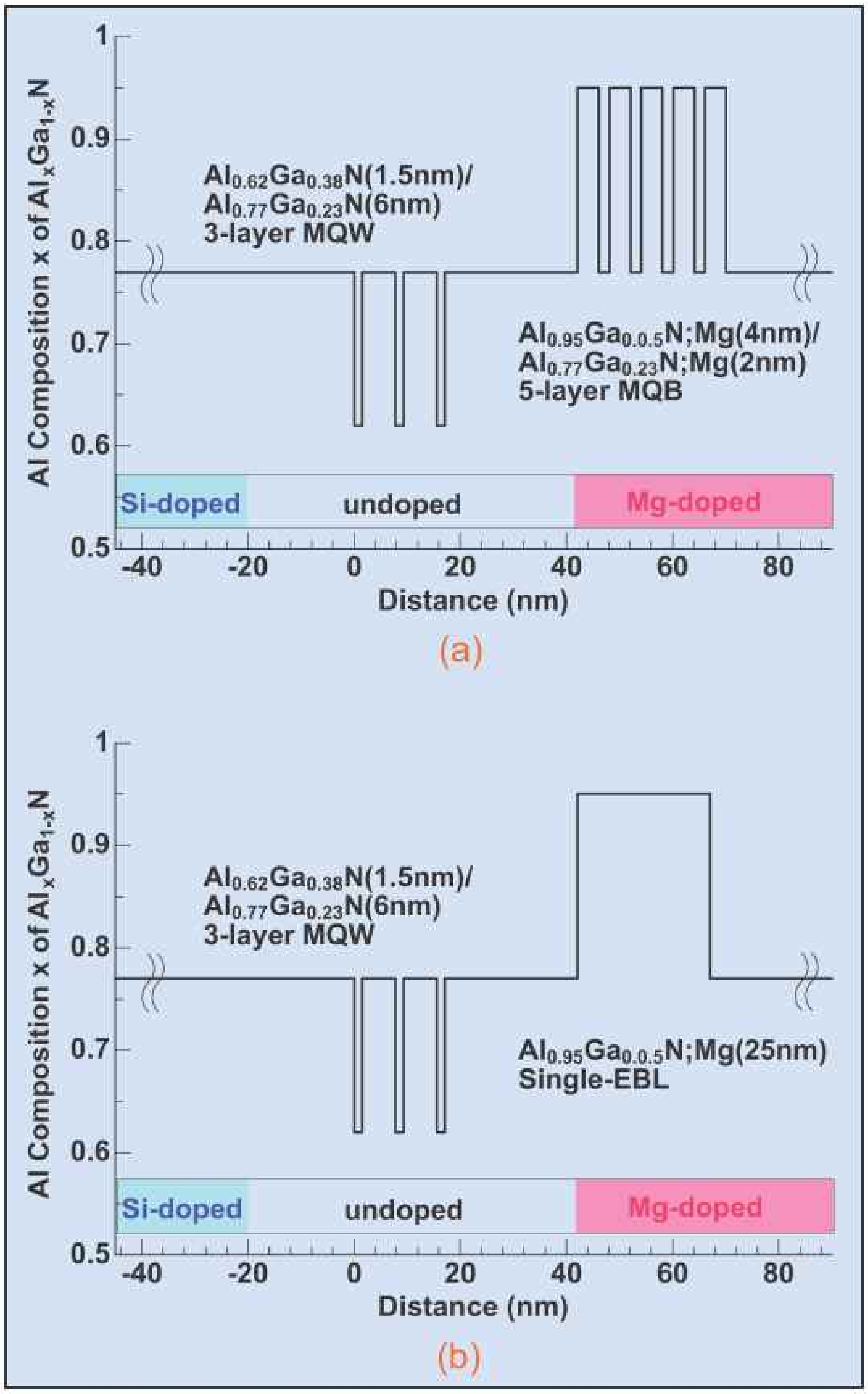

Figure 10. Compositions and doping profiles of AlGaN layers used for 250nm AlGaN QW LEDs produced by Saitama et al with MQB (a) and single-barrier EBLs (b).

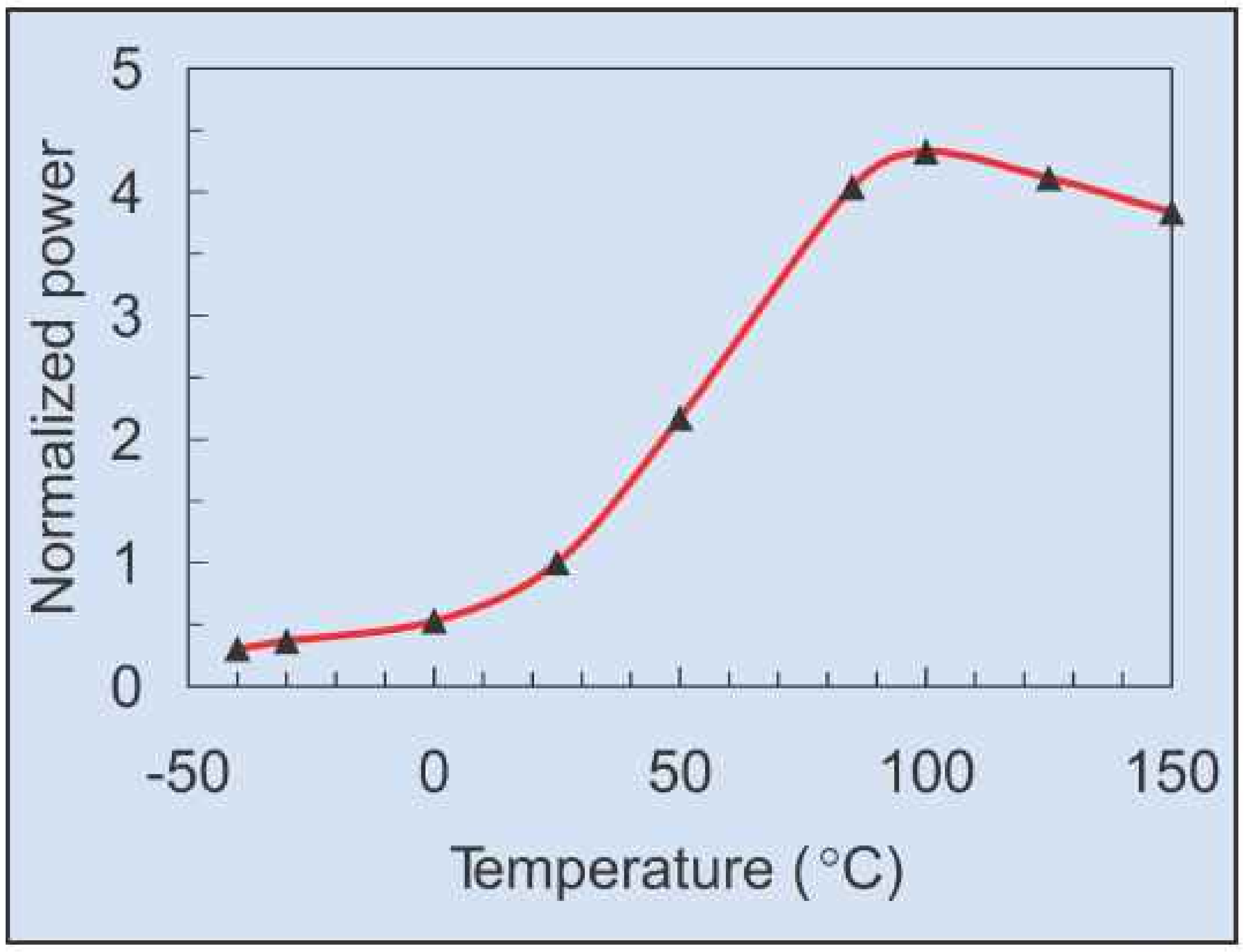

Figure 11. Temperature dependence of normalized output power of Nichia UV LED from –40 to 150°C.

Packaging and modules

Packaging is also a key component for developing UV LED sources. While much of the academic research on DUV LEDs has centered on increasing the quantum efficiency of the chip, commercial producers also have to consider the problem of extraction of the precious photons into the external world. In addition, thermal control is a particular problem for UV LEDs since the emissions depend on band-to-band transitions, rather than the less temperature-dependent localized states used in blue InGaN LEDs.

In fact, Nichia has found that in DC operation, where self-heating can occur, some devices actually produced more output power, achieving maximum power after about a minute [7]. This effect was probably due to the self-heating ionizing the acceptor doping in the p-type region, releasing holes (thermally enhanced p-type activation). Indeed, studies of the temperature dependence of the device (Figure 11) suggest that it is most efficient around 100°C. Using pulsed currents (50μs width, 2kHz repetition), the output power was 0.69mW, 28% that achieved with DC operation.

It is estimated that deep ultraviolet devices have extraction efficiencies less than 10% due to light absorption in GaN contact layers and low reflection ratio from p-type layers. Thus, some of the tricks used for increasing extraction in longer wavelength LEDs are not available (as yet). For example, putting the LED in a reflecting cup to redirect photons emerging from the bottom of the chip is not of much use where the p-contact layers of the chip heavily absorb the ultraviolet radiation passing through. While using p-AlGaN might allow greater extraction efficiency of ultraviolet radiation, it would severely reduce hole concentrations and hence injection efficiency, since the Mg acceptor levels become deeper with increasing aluminum content [12].

A leading example of a commercial producer is Sensor Electronic Technology (SET). This US company carries out its own packaging R&D and has both device fabrication and packaging facilities at its site in Columbia, South Carolina. The firm finds that the majority of its more than 1000 customers have no experience in the use of semiconductors, so it has to be a solutions provider.

SET also extracts UV light that is 'waveguided' along the active layers, emerging from the edges of the chip (Figure 5). The company would also like to extract light emitted through the p-type contact. The researchers at SET are working on a new device structure that has the potential to more than double the extracted light.

For thermal control, SET's ultraviolet LEDs use a heatsink. Further strategies being developed include improving the doping to reduce the resistance of the injection layers. Larger-area devices to reduce the current densities are another strategy for reducing self-heating.

With US National Science Foundation (NSF) funding, the firm has developed a phase I prototype portable all-LED 273nm water sterilization unit with capability of 5-log (99.999%) virus inactivation/removal with a 0.5 liter/min flows and 4-log (EPA Ground Water Rule, www.epa.gov/safewater/disinfection/gwr/index.html) with 1 liter/min. UV radiation can also be used for surface sterilization.

Nichia has also tested a multi-LED arrangement consisting of 26 devices (2x13), which produced an output of 223mW with pulse injection (5ms, 10Hz repetition) at 1.85A. Measurements were carried out with water cooling. The maximum current was limited by the ability to remove heat across the bonding interface between the LED chip and sub-mount. The maximum current in DC operation was 460mA (~35mA/die), giving a UV output of 60mW. ■

The author Mike Cooke is a freelance technology journalist who has worked in the semiconductor and advanced technology sectors since 1997.

References

1. Kolbe et al, International Conference on Nitride Semiconductors (ICNS), Session BB6, 2009
2. Max Shatalov et al, ICNS, Session BB2, 2009
3. Hirayama et al, ICNS-8, BB4, 2009
4. W. Sun et al, Appl. Phys. Lett., vol96, p061102, 2010
5. Hideki Hirayama et al, Appl. Phys. Express, vol3, p031002, 2010
6. Tsukada et al, ICNS-8, BB5, 2009
7. Akira Fujioka et al, Appl. Phys. Express, vol3, p041001 2010
8. Krishnan Balakrishnan et al, Jpn. J. Appl. Phys., vol49, p040206, 2010
9. www.dowa.co.jp/en/ir/pdf/news2009/release100315_e.pdf
10. Hideki Hirayama et al, Phys. Status Solidi A 206, p1176, 2009
11. Shibata et al, physica status solidi (c), vol0, p2023, 2003
12. See Mike Cooke, "Polarization technology for HEMTs and LEDs", Semiconductor Today, this issue