ACS Photonics
pubs.acs.org/journal/apchd5
Perspective

Bright Future of Deep-Ultraviolet Photonics: Emerging UVC Chip-Scale Light-Source Technology Platforms, Benchmarking, Challenges, and Outlook for UV Disinfection

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Cite This: *ACS Photonics* 2022, 9, 1513–1521
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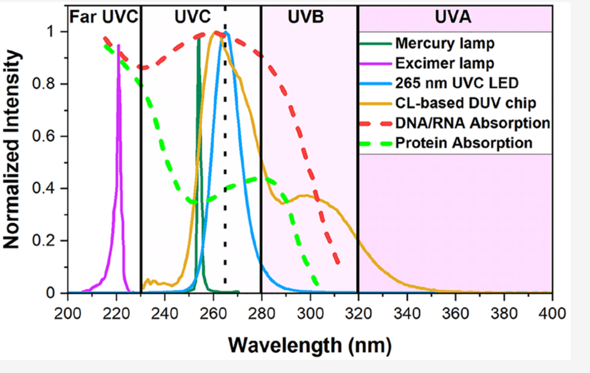
ABSTRACT: The COVID-19 pandemic has generated great interest in ultraviolet (UV) disinfection, particularly for air disinfection. Although UV disinfection was discovered close to 90 years ago, only very recently has it reached the consumer market and achieved much acceptance from the public, starting in the 2000s. The current UV light source of choice has been almost exclusively a low-pressure mercury vapor discharge lamp. Today, however, with emerging deep-UV (DUV) chip-scale technologies, there has been a significant advancement, along with ever-increasing interest, in the development and deployment of disinfection systems that employ compact devices that emit in the deep-UV spectral band (200–280 nm), including UV light-emitting diodes (LEDs) and cathodoluminescent (CL) chips. This perspective looks into competing UV technologies (including mercury lamps and excimer lamps as benchmarks) on their optical merits and demerits and discusses the emerging chip-scale technologies of DUV electroluminescent and cathodoluminescent devices, comparing them against the benchmarks and providing an overview of the challenges and prospects. The accelerating progress in chip-scale solutions for deep-UV light sources promises a bright future in UV disinfection.

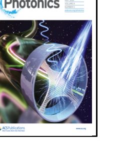


KEYWORDS: *mercury lamp, excimer lamp, UVC LEDs, cathodoluminescent chips, germicidal efficiency*

Ultraviolet (UV) radiation, which is part of the electromagnetic spectrum, can be divided into three spectral bands comprising the UVA (320–400 nm), UVB (280–320 nm), and UVC (200–280 nm) bands; UVC is also commonly known as deep-UV (DUV) (Figure 1a). UVA is nearly visible and is known to cause skin damage. Being a slightly shorter waveband, UVB is a major factor causing sunburn in the daylight as well as causing skin damage. Both UVA and UVB easily enter the earth's atmosphere, are present in daylight, and are harmful to our skin because of their long penetration depth into the human tissue (Figure 1b). On the other hand, UVC wavelengths are blocked by ozone in the earth's atmosphere and are not present in sunlight at the surface of the earth, which means pathogens have not evolved defenses against UVC radiation. Therefore, because of the germicidal effectiveness of the UVC wavelengths, this phenomenon is also known as ultraviolet germicidal irradiation (UVGI).[1] UVGI can destroy the ability of microorganisms to reproduce by causing photochemical changes in their nucleic acids, which destructively impairs reproducibility and thus renders them inactive (inset of Figure 1a). All wavelengths in the UV range are known to cause some photochemical effects; high-energy photons in the UVC range are specifically damaging to cells because they are absorbed by DNA and RNA (DNA/RNA) as well as proteins (inset of Figure 1a). The germicidal effectiveness peaks at ~260–265 nm, which also corresponds to the peak of UV absorption for bacterial DNA/RNA (Figure 1a).[1,2] Thus, technically any UV source emitting in the 260–265 nm band in principle will be more effective for disinfection. Spectral comparisons among various UVC light sources in reference to the standard absorption spectra of DNA/RNA (alternatively referred to as germicidal effectiveness curve (GEC)) and the absorption spectrum of proteins are shown in Figure 1c.

Looking at Figure 1c, it can be seen that low-pressure mercury lamps exhibit high germicidal effectiveness because they radiate the majority (~85%) of their optical output at a wavelength of 254 nm, which is quite close to the peak of GEC (260–265 nm). Also recently, excimer lamps are becoming increasingly popular for their emission at 222 nm, which is considered to be safer because of their limited penetration depth in human tissue

Received: January 6, 2022
Revised: April 14, 2022
Accepted: April 18, 2022
Published: April 28, 2022



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ACS Photonics 2022, 9, 1513–1521

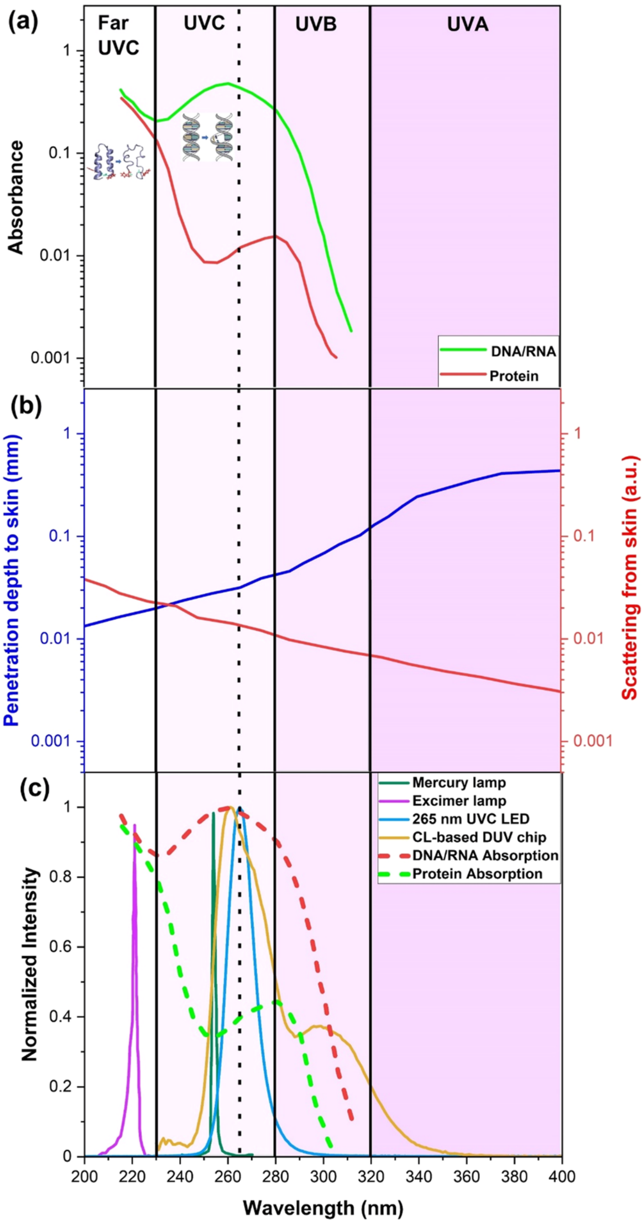

Figure 1. (a) Standard absorption spectrum of DNA and RNA (also known as germicidal effectiveness curve) peaking at 265 nm (indicated by the dashed vertical line) along with the absorption spectrum of proteins, both increasing toward further shorter wavelengths.[1,2] (b) Penetration depth into the human skin and scattering from the human skin across the UV and its values at specific wavelengths of interest are ~18 μm (222 nm), ~27 μm (254 nm), and ~32 μm (265 nm).[7,8] (c) Comparison of various UVC light sources with the standard absorption spectra of DNA/RNA and proteins.

(Figure 1b). The peak emission wavelength of UVC LEDs can be tuned by varying the Al concentration in $Al_xGa_{1-x}N$, and recently UVC LEDs emitting at 265 nm have been achieved, although at low efficiency levels (~1−3%).[3−6] On the other hand, the emission spectrum generated by cathodoluminescent (CL) DUV chips can be wide, fully overlapping with the germicidal UVC range, and can be tuned to peak in the spectral band of 260−265 nm.

Human skin is commonly divided into three layers: the top layer called the epidermis, the middle layer called the dermis, and the bottom layer known as the hypodermis. The stratum corneum is a dead skin layer on the top of the epidermis with a thickness of 10−20 μm.[7,8] The total thickness of the epidermis layer lies between 50 and 150 μm, whereas the thickness of the dermis layer is ~1−4 mm.[7,8] It is clear from Figure 1 that the 254 nm UVC range is mostly absorbed by the DNA/RNA, and it can penetrate deeper into the epidermis layer of the human skin and damage the DNA in the skin cells, which could, in turn, induce cancer. On the other hand, the 222 nm UVC range is highly absorbed by both proteins and DNA/RNA and will be mostly absorbed by the stratum corneum (dead layer) of the skin, which increases the effectiveness of the 222 nm UVC band compared to the 254 nm UVC against microbes. The germicidal efficiency is known to vary with wavelength and is described by the GEC peaking around 265 nm (denoted by the vertical dashed lines in parts a−c of Figure 1). Also, because of the popularity of excimer lamps, the deep-UV wavelength range of 200−230 nm is further specified as the far-UVC.

DEEP-ULTRAVIOLET LIGHT SOURCES

The first scientific report on the germicidal effects of UV radiation was published in the year 1877.[9] By the year 1929, UV dosages required to disinfect various bacteria and fungus had been reported.[10−12] The 1930s saw the implementation of UV systems in hospital settings to control infections,[13−16] and it was acknowledged after 20 years that these systems were effective in disinfecting both air and surfaces. Although UVGI systems had been in use in hospitals for decades, only very recently, in 2003, did the Centers for Disease Control and Prevention (CDC) formally endorse that these systems could be used in hospitals under certain guidelines.[17] Low-pressure mercury (Hg) lamps have been exclusively used for disinfection purposes for over 90 years and dominate the germicidal UV market today. However, now we observe growing health concerns associated with the use of toxic mercury, and the Minamata Convention has been implemented across 128 countries to phase out completely or at least phase down Hg-based lamps for health and environment-related issues.[18] This has been strongly motivating the rapid development of various mercury-free DUV technologies for disinfection purposes. Promising DUV technologies include UVC LEDs and CL-based DUV light chips, which are both chip-scale solutions, as well as excimer lamps, which are not chip-based and are indeed based on old technology but have been recently attracting interest for their far-UVC capability. Figure 2 directly compares the sizes of these different light sources and contains the schematics of all of the DUV light sources discussed in this Perspective. We will discuss these technologies in the following sections along with their merits and demerits.

Mercury Lamps for Benchmarking in Deep-UV. Mercury lamps have enjoyed a monopoly in the disinfection market for over 90 years. They are often referred to as UV lamps or amalgam lamps. The two most common types are medium-pressure (MP) and low-pressure (LP) mercury vapor lamps defined by the mercury gas pressure in them. MP UV lamps contain mercury gas at a pressure of ~1000 Torr, whereas for LP UV lamps the pressure is ~10 Torr. MP UV lamps have a polychromatic emission pattern with an intense peak around 365 nm. On the other hand, LP UV lamps have monochromatic emissions centered around 254 nm, as shown in Figure 1c. Therefore, LP UV lamps have found usage in disinfection because their emission is close to the peak of the germicidal curve. LP UV lamps consist of a UV-transmitting glass envelope, a pair of electrodes, and a mercury amalgam. A schematic of a standard LP mercury lamp is shown in Figure 2d. The electric

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ACS Photonics 2022, 9, 1513−1521

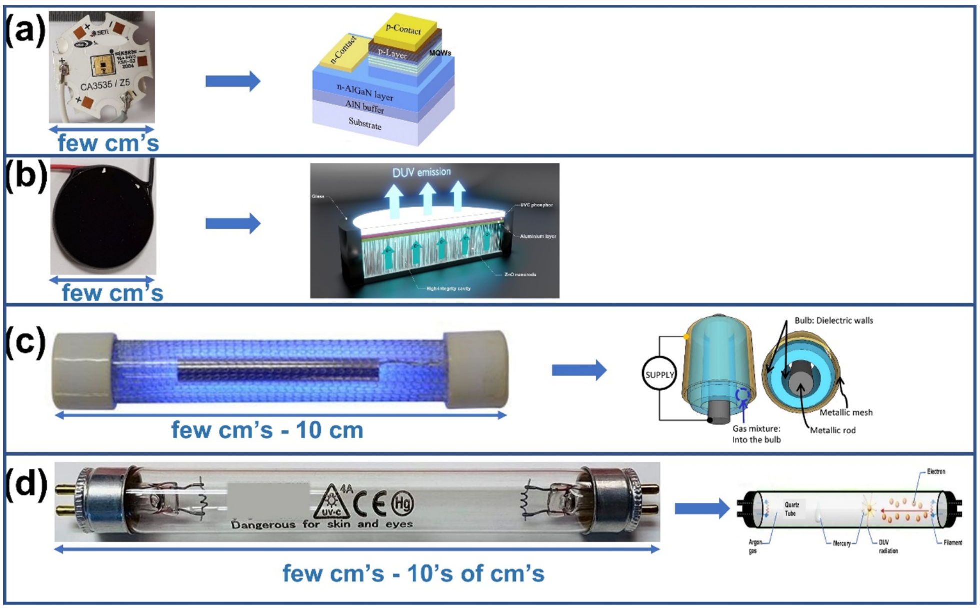

Figure 2. Size comparison (on the same scale) and schematics of the following: (a) UVC LED. Adapted with permission from ref 19. Copyright 2017 Elsevier. (b) CL-based DUV chip. Reprinted with permission from ref 20. Copyright 2021 John Wiley and Sons. (c) Excimer lamp. Adapted with permission from ref 21. Copyright 2012 IEEE. (d) Mercury lamp. Adapted with permission from ref 22. Copyright 2014 Elsevier.

current provided by the ballast passes through the electrodes and heats the mercury vapor, which stimulates electronic transitions and causes UV emission. In the LP UV lamps, ~60% of the electrical input power is converted to light, of which ~85% occurs near 254 nm.[23] The typical efficiencies of the LP UV lamps are in the range of ~15−30% with a possibility of variation depending on ambient operating conditions.[24]

Mercury lamps have been the mainstream option for DUV light sources for many years. However, these lamps contain mercury, which is highly toxic to humans and is environmentally harmful. Therefore, these light sources cannot be used safely in settings close to human end-consumers, for example, in healthcare facilities and public places. Besides, these lamps are undesirably large (tens of centimeters) and suffer from long warm-up times (typically minutes) before radiating DUV, making them impractical in certain applications. The adverse effects of mercury on human health and the environment have also been acknowledged, worldwide leading to the Minamata Convention on mercury.[18] In 2017, this convention came into force with a target to stop or reduce the use of mercury in existing processes, resulting in robust demand for alternative DUV light sources.

Excimer Lamps As a Far-UVC Source. Excimer lamps are based on a mature technology whose origin goes back to the demonstration of the first excimer laser in the year 1970.[25,26] Excimer lamps found use in a large number of applications including substrate cleaning, UV curing, surface modification, material deposition, and water and air purification. More recently, after the implementation of the Minamata Convention, excimer lamps have become increasingly popular as an alternative to mercury-based UV lamps.[27,28] Excimer lamps provide high-intensity far-UVC radiation generated by decaying excimer complexes formed in various nonequilibrium discharges.[25] A schematic of a coaxial excimer dielectric barrier discharge (DBD) far-UVC lamp is shown in Figure 2c. Different gas mixtures create different light frequencies; thus, the spectra of the excimer lamp are defined by the working excimer molecule. For example, an excimer lamp filled with a mixture of krypton (Kr) and chlorine (Cl) gas primarily makes 222 nm light when energized, whereas Kr and Br together will emit at ~207 nm.

Excimer lamps are considered to be safer than mercury lamps because the far-UVC wavelength range has a very limited penetration depth in the human skin (see Figure 1b). Nonetheless, this limited penetration is still much larger than the size of viruses and bacteria; therefore, far-UVC light is as efficient at killing pathogens as conventional germicidal UV light.[29,30] However, far-UVC light, because of its limited penetration, cannot reach or damage living cells in human skin or eye, in contrast to conventional germicidal UV light, which can be a health hazard.[28,31,32] However, until now this claim has not been acknowledged by governments or authorities worldwide and is still under debate. More research is needed to conclude that excimer lamps are safer than conventional UVC light sources. Also, there are a lot of unknowns about excimer lamps, especially in terms of their germicidal efficacy on different pathogens.

■ EMERGING CHIP-SCALE UVC TECHNOLOGIES

Electroluminescent Devices: UVC LEDs. UV light-emitting diodes (LEDs) are compact, environmentally friendly (mercury-free), solid-state light sources with many advantages over mercury lamps. A UVC LED can be deployed in places where space does not permit regular mercury lamps. This is a carefully engineered p−i−n junction that emits in the UV range when forward-biased. A schematic of a typical UVC LED is shown in Figure 2a. In principle, UV LED technology is based on the conventional LED technology used for general lighting. DUV LEDs are built using the same basic material system of III-nitrides as are blue and near-UV LEDs, except that, to shift the emission wavelength from the blue (typically 440−460 nm) toward the UV, In (indium) in InGaN must be replaced with increasing amounts by Al (aluminum) in AlGaN. Therefore, to make an LED operating in the DUV spectral region, a relatively large portion of Al must be used. The problem with Al is fundamentally challenging because Al is a smaller atom than In

https://doi.org/10.1021/acsphotonics.2c00041
ACS Photonics 2022, 9, 1513−1521

and will not have a good match in the crystal lattice. Therefore, this inherent mismatch leads to major lattice stress and inevitably to crystal defects, as well as difficulty in p-type doping, which in turn leads to a decrease in efficiency. By tuning the right Al concentration, UVC LEDs will emit at the optimum wavelength (~265 nm) for maximizing germicidal effectiveness, as shown in Figure 1c.

The current benchmarks for UVC LEDs in terms of external quantum efficiency (EQE) are shown in Figure 3. EQE is defined as the ratio of the number of photons emitted from the LED to the number of electrons passing through the device. In other words, EQE is the product of internal quantum efficiency (IQE), carrier injection efficiency (CIE), and light extraction efficiency (LEE). The maximum EQE achieved for AlGaN-based LEDs is 20.3% at 275 nm.[44] The EQEs of commercially available AlGaN-based UVC LEDs are much lower compared to the benchmarked GaN-based blue and green LEDs, which is caused by high dislocation densities (poor quality of AlGaN material), low hole concentrations (p-type doping problem in AlGaN), and low LEE.[3,6] Furthermore, we see an order of magnitude difference in the EQE of UVC LEDs below the peak of the germicidal effectiveness curve (265 nm), as seen in Figure 3. The EQE drops sharply below 4% at wavelengths shorter than 265 nm (obtained by increased Al content), stemming from the deterioration in the crystalline quality of the AlGaN material, the difficulty of p-type doping processes, and the degradation of TE-mode polarization. p-type doping is a major technical problem in obtaining high-efficiency UVC LEDs at higher Al doping concentrations. A considerable research effort is being put into improving the EQE of UVC LEDs, and it is anticipated that high-efficiency UVC LEDs will be realized by mitigating these difficulties.

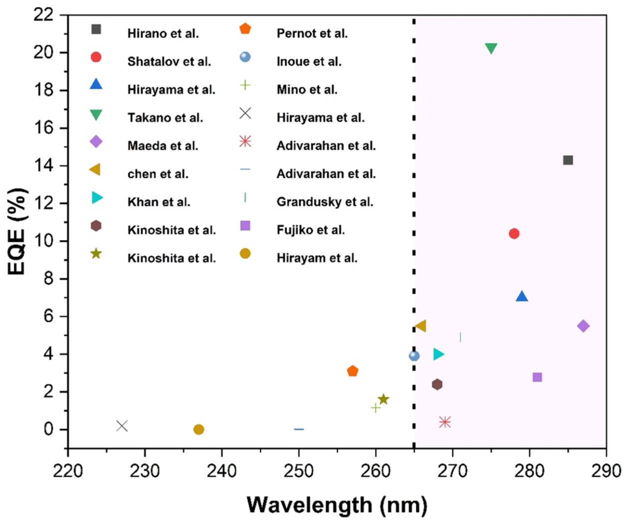

Figure 3. State-of-the-art EQE of UVC LEDs.[33−51] The dashed vertical line shows the peak of the germicidal effectiveness curve, which serves as a reference for assessing EQE below and above this wavelength (265 nm).

Wall-plug efficiency (WPE) is another key performance parameter for UV LEDs. WPE corresponds to the ratio of the optical output power and the electrical input power and is expressed as[4,6]

$$\mathrm{WPE} = \frac{P_{\mathrm{out}}}{IV} = \mathrm{EQE} \times \eta_{\mathrm{el}} \quad (1)$$

where η_{el} is the electrical efficiency, P_{out} is the output optical power, I is the operating current, and V is the operating voltage of the LED. The WPE of UVC LEDs is further discussed for comparison in the last section of the paper.

Cathodoluminescent Devices. *System-Level Electron-Beam-Driven UVC Light Sources.* One possible approach to overcome the troublesome nature of p-type doping processes in UVC LEDs and achieve DUV light emission is by using the electron-beam (EB)-pumping technique. In EB-pumped DUV light sources, normally thermal electron-gun (e-gun) emitting via thermionic emission is used as the electron emitter. Recently, because of the compactness of EB-pumped light sources for practical applications, the thermal e-gun has been replaced with cold-field emitters, which emit on the principle of field emission (via a quantum mechanical process known as quantum tunneling). In both cases, the electrons are accelerated in a high vacuum by the applied electric field toward the anode. The anode can be AlGaN multiple quantum wells (MQWs) that generate DUV light when hit by these electrons (a photon emission process via excitation of high-energy electrons known as cathodoluminescence). Such EB-pumped UVC light sources are also called cathodoluminescent (CL) light sources. Compared with UVC LEDs, EB-pumped DUV sources offers numerous advantages including (i) the complete absence of a p-type layer in the structure, (ii) a reduction in the absorption of the emitted light because of a simple structure, and (iii) a basic thin-film anode for epitaxial growth, making it suitable for the mass fabrication. Besides AlGaN MQWs, various UVC phosphors have been investigated as potential anodes for EB-pumped DUV light sources.

The development history of EB-pumped DUV light sources is less than 10 years, but the progress made in the power conversion efficiency (PCE) is quite significant (Figure 4). The power conversion efficiency (PCE) is defined as the output optical power to the input electrical power and is expressed as[52]

$$\mathrm{PCE} = \frac{P_{\mathrm{out}}}{IV_{\mathrm{A}}} = (\mathrm{EQE}) \times \eta_{\mathrm{eh}} \quad (2)$$

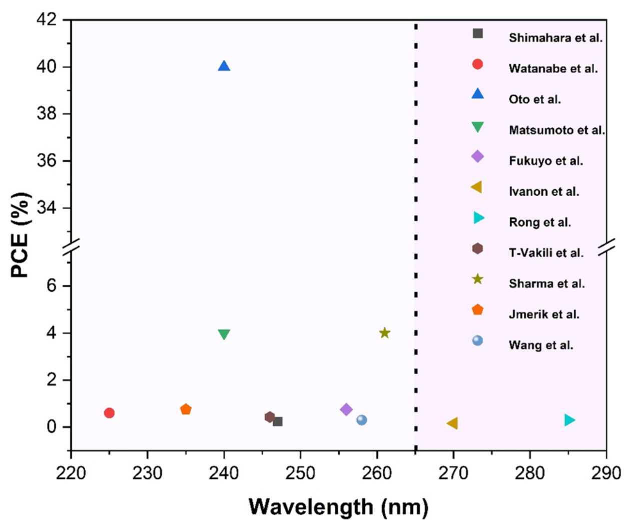

Figure 4. State-of-the-art PCE of EB-driven DUV light sources.[20,52−61] The dashed vertical line denotes the peak of the germicidal effectiveness curve, which serves as a reference for evaluating PCE below and above this wavelength (265 nm).

https://doi.org/10.1021/acsphotonics.2c00041
ACS Photonics 2022, 9, 1513−1521

Table 1. Compact Packaged CL-Based DUV Devices Fabricated Using Cold Cathodes

cathode	anode	EB energy	output power (mW)	PCE (%)	wavelength (nm)	refs
Spindt field-emission array	hBN powder	9.0 keV, 100 μA	0.2	0.6	225	54
graphene nanoneedles	AlGaN quantum wells	7.5 keV, 80 μA	20	3−4	240	53
ZnO nanorods	UVC phosphor ($Lu_2Si_2O_7$:Pr^{3+})	6.5 keV, 90 μA	20	4	261	20

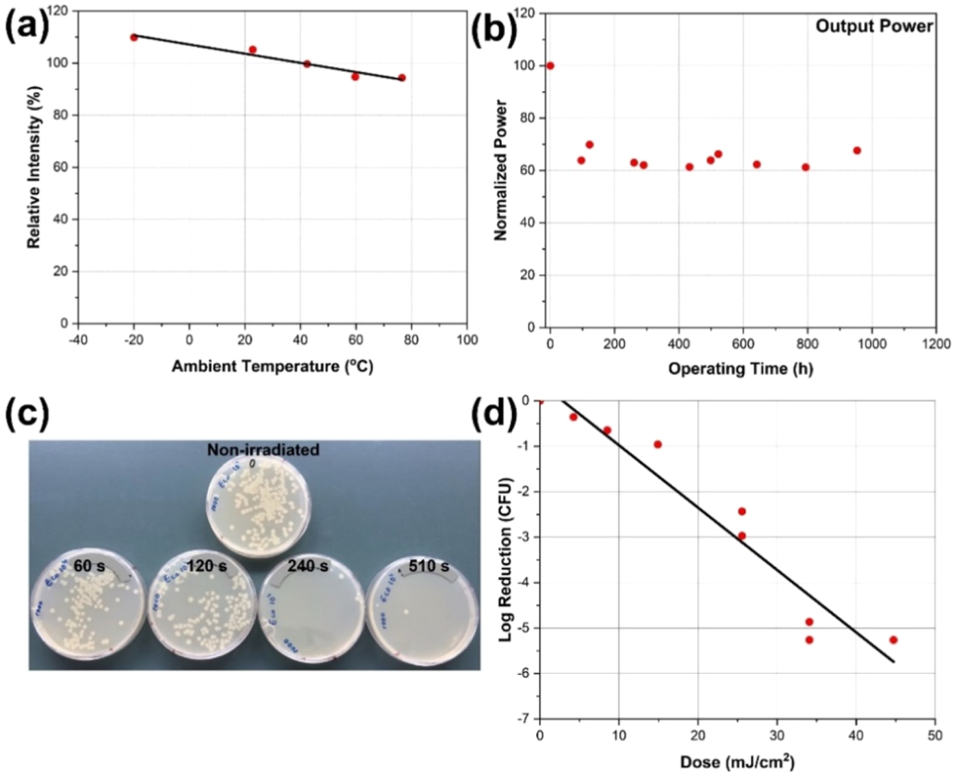

Figure 5. Chip performance at varying operating (a) temperatures, (b) times (lifetime test), (c) *E. coli* bacteria before and after DUV irradiation, and (d) log-reduction obtained for *E. coli* bacteria using these DUV chips. Adapted with permission from ref 20. Copyright 2021 John Wiley and Sons.

where η_{eh} is the yield of converting irradiated electrons into electron−hole pairs, P_{out} is the output optical power, I is the irradiated current, and V_A is the accelerating voltage of EB sources. The most remarkable result reported by Oto et al.[52] is the demonstration of a 100 mW optical output with a PCE of ∼40% from EB-pumped (e-gun) AlGaN/AlN MQWs emitting at ∼240 nm operated inside a vacuum chamber. The authors attributed such a high PCE to the strong carrier confinement provided by high-quality AlGaN/AlN QWs as well as to the appropriate design of the sample structure for EB excitation. Other than ref 52, in most of the cases, the PCE reported is currently less than ∼1% for all DUV wavelengths at the system level (Figure 4). Although the performance levels of such EB-pumped DUV light sources have progressed, many challenges still exist in the development of these light sources for practical applications. First, the size miniaturization of EB-driven DUV light sources is critical for many practical applications. More studies are needed using cold cathodes instead of thermal cathodes in this regard. Second, a requirement of a high vacuum to provide high-energy field-emission electron sources raises the difficulty at the system level. Third, to obtain a high carrier injection efficiency, it is imperative to match the thickness of the MQW structure to the EB penetration depth. A lot of understanding has been gained in the past decade on the relationship between the EB penetration depth and the MQW thickness. The efficiencies of EB-pumped DUV light sources may surpass those of UVC LEDs and possibly those of excimer lamps provided that other phosphors with high efficiencies are developed in the UVC wavelength range. The emission wavelength can be tuned in EB-pumped DUV light sources by changing the anode (the concentration of Al in AlGaN MQWs or the composition of the UVC phosphor).

Chip-Scale Integrated Cathodoluminescent UVC Light Sources. For practical applications, in addition to the required high PCE, EB-pumped DUV light sources need to be made compact to compete with UVC LEDs.[3,62] The size miniaturization is the biggest challenge for CL-based DUV light sources. Therefore, in this section, we focus only on the compact packaged CL-based devices fabricated using field-emission cold cathodes (see Table 1). Watanabe et al.[54] reported a CL device with a PCE of 0.6% using hexagonal boron nitride (hBN) far-ultraviolet (225 nm) fluorescent powders and a Spindt field-emission array cold cathode. Matsumoto et al.[53] made a notable improvement in the PCE (∼4%) by demonstrating a handheld device emitting at 240 nm with 20 mW power obtained by combining $Al_{0.7}Ga_{0.3}N$/AlN MQWs and graphene nanoneedle cold cathodes. Recently, our group has demonstrated DUV light chips emitting at 261 nm with an output power ≥20 mW at a PCE ∼4% based on a novel chip-based architecture.[20] In this architecture, as shown in Figure 2b, the electron-emitter cold cathode and the DUV photon-emitter anode are integrated inside a compact, high-integrity sealed vacuum cavity for

https://doi.org/10.1021/acsphotonics.2c00041
ACS Photonics 2022, 9, 1513−1521

Table 2. Competitive Analysis of the Existing State-of-the-Art Technologies: Mercury Lamps, Excimer Lamps, UVC LEDs, and CL-Based DUV Chips

competitive analysis	Hg lamps (254 nm)	Excimer lamps (222 nm)	CL-based DUV chips (<265 nm)	UVC LEDs (265 nm)
technology	mercury lamps	Kr−Cl gas	field-emission (cathodoluminescence)	AlGaN LEDs
germicidal efficiency (log reduction)	log 6 (99.9999%)	log 3 (99.9%)	log 6 (99.9999%)	log 3 (99.9%)
efficiency	∼15−35%	∼5−15%	∼4−5%	∼1−3%
operational temperature range	20−60 °C	0−100 °C	−20 to 100 °C	0−80 °C
instant ON/OFF	no	yes	yes	yes
cost	high (continues ON)	high (continues ON)	low (intermittent operation)	low (intermittent operation)
environmentally friendly	no	yes	yes	yes

efficient field-emission from the cathode, resulting in efficient cathodoluminescence from the anode. The DUV chips after packaging are <30 mm (diameter) in size with a 4 mm thickness (Figure 2b), allowing complete design freedom like UVC LEDs. We also found that the performance of the chip remains similar under different temperature conditions (−20 to 80 °C), which will be useful for a variety of applications requiring operation at extreme temperatures or a large variation of temperature during operation (Figure 5a). Additionally, the lifetime of the tested chips is ∼500 h and is expected to be longer after further optimizations (Figure 5b). Moreover, we also found log 6 (99.9999%) germicidal efficacy using these DUV chips owing to the spectral overlap of the phosphor's CL spectrum and the standard germicidal effectiveness curve (GEC) (Figure 5c and d). Such EB-driven DUV light sources are an emerging field giving tough competition to UVC LEDs. It is expected that, if the synthesis of UVC phosphors with high efficiency or growth of high-quality defect-free AlGaN/AlN MQWs is realized, the fabrication of compact EB-pumped DUV light sources with higher power and efficiencies will be rapidly developed.

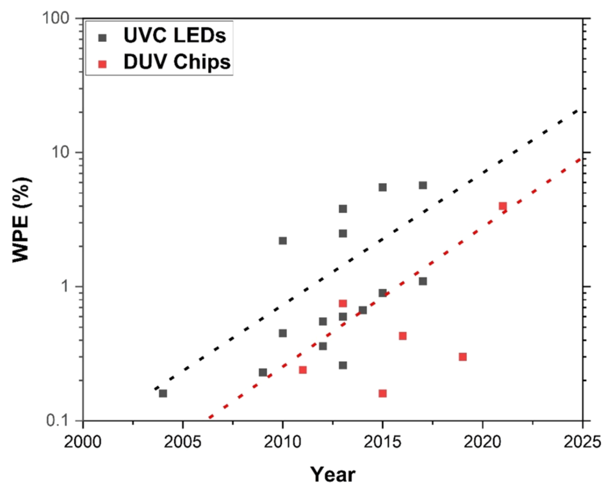

Figure 6. WPE (PCE) of UVC LEDs and CL-based DUV chips for 240−280 nm UVC emission band. The dashed lines provide an estimate of the WPE of UVC LEDs (black line) and CL-based DUV chips (red line) up to the year 2025.

■ COMPARISON, CHALLENGES, AND FUTURE PROSPECTS

All of the DUV light sources have their own merits and demerits. Hence, choosing the right one depends on the competitiveness they offer over other UVC light sources in terms of compactness, efficiency, temperature stability, and germicidal efficacy. Table 2 summarizes the comparison between the four different technologies (mercury lamps, excimer lamps, UVC LEDs, and CL-based DUV chips) discussed in this brief review. Although mercury lamps have several disadvantages, they still enjoy popularity in the market because of their availability. However, the deployment of mercury lamps must scale down because of the Minamata Convention adopted by 128 countries. Thus, UVC LEDs, DUV chips, and excimer lamps will play a bigger role in the future UV-disinfection market. UVC LEDs share the same platform as the III-nitride material system with blue LED technologies. Although AlGaN-based UVC LEDs with an impressive EQE of 20.3% at 275 nm are achieved, EQE drops drastically with decreasing wavelength, resulting from multiple factors. Thus, there are still many challenges in the development of high-efficiency UVC LEDs. Nonetheless, there seems to be no fundamental blockade preventing the development of high-efficiency UVC LEDs, and one can expect these LED's performance levels to be like those of InGaN-based blue LEDs soon.

Figure 6 shows the WPE reported for UVC LEDs and PCE for CL-based DUV chips in the 240−280 nm emission bands and its prediction up to the year 2025. The 240−280 nm emission band is chosen because this range is considered the most effective for UV-based disinfection. By definition, we can directly correlate the PCE of e-beam-pumped DUV light sources with the WPE of UVC LEDs. The expected performance of UVC LEDs based on the trajectory of preceding developments is projected to reach WPE ∼20% for 270−280 nm wavelength, whereas for the 240−270 nm band it is expected to reach WPE ∼10% by 2025 (Figure 6).[3,4,6] The main factors driving the WPE improvement will be the increased internal quantum efficiency, reduced operating voltages, and enhanced light extraction. On the other hand, recently EB-pumped DUV light sources (CL-based DUV chips) have made faster progress compared to UVC LEDs. EB-pumped AlGaN-based DUV light sources with an impressive WPE (PCE) of 40% have been demonstrated at a wavelength of 238 nm.[52] Interestingly, such high efficiency was not reported by any other research group; recently, a few researchers demonstrated portable light sources with efficiency levels as high as ∼4−5% at wavelengths below 260 nm, which is relatively higher in comparison to UVC LEDs in this wavelength range.[20,53] Our recent report has also demonstrated that CL-based DUV chips possess an exceptional germicidal performance level of log 6 (99.9999%) as opposed to log 3 (99.9%) level for germicidal efficiency of UVC LEDs. The CL-based devices also provide the instant ON/OFF, low-temperature dependence, and compactness offered by UVC LEDs.[20] It is expected that, if DUV phosphors with high efficiency are developed, CL-based DUV chips offer the potential to overtake UVC LEDs (Figure 6).

Figure 6 also shows the WPE (PCE) reported for CL-based DUV chips in the 240−280 nm emission bands, which is projected to rise to 10% by 2025. Especially for the 240−270 nm wavelength, currently the EB-pumped DUV chips have an edge

https://doi.org/10.1021/acsphotonics.2c00041
ACS Photonics 2022, 9, 1513−1521

over the UVC LEDs and offer higher performance as of now. Also, if efficient phosphors in the far-UVC range are developed, DUV chips possibly challenge the excimer lamps, too. However, further optimization and advancement in the device structure, fabrication, and high-efficiency UVC phosphor/defect-free AlGaN will be prerequisites to demonstrate further higher-performance CL-based DUV devices for practical applications. Finally, excimer lamps are getting much attention nowadays because of their potential for safety when used in open spaces over the other DUV light sources, which allows them to be used in public places. However, a lot more research efforts in terms of both the germicidal efficacy and the safety aspects are required before we use them freely in public settings.

■ CONCLUSIONS

In conclusion, although UVC LEDs offer the advantages of being mercury-free, compact, instant-ON, and low-cost, especially in the region of 260−265 nm, which is the most effective range for UV disinfection, the efficiency of these UVC LEDs is still low for practical applications.[4,6] CL-based DUV chips are in the initial stage of development, but the WPE (PCE) reported is already in the range of ∼4−5% for the packaged chips for wavelengths shorter than 265 nm. Additionally, these chips also offer similar features offered by UVC LEDs. Although excimer lamps emitting in far-UVC are based on mature technology, only recently have they attracted much interest because of their potential for safety in human settings over other DUV light sources. Furthermore, studies are needed to evaluate their germicidal effectiveness on various pathogens. Overall, besides mercury lamps, all other technologies coexist in the market based on their competitiveness and trade-offs in terms of compactness, high efficiency, improved germicidal efficacy, wide operation-temperature range, long operational lifetimes, and better safety aspects.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work is an outcome of a joint project entitled “Next-Generation Ultralow-Cost High-Efficiency Eco-Friendly Lamps” between LightLab AB, Sweden, and NTU, Singapore. H.V.D also acknowledes support from TUBA.

■ REFERENCES

(1) Kowalski, W. *Ultraviolet Germicidal Irradiation Handbook*; Springer: Berlin/Heidelberg, 2009; DOI: 10.1007/978-3-642-01999-9.

(2) Harm, W. *Biological Effects of Ultraviolet Radiation*; Cambridge University Press: United Kingdom, 1980.

(3) Li, D.; Jiang, K.; Sun, X.; Guo, C. AlGaN Photonics: Recent Advances in Materials and Ultraviolet Devices. *Adv. Opt. Photonics* **2018**, *10* (1), 43.

(4) Amano, H.; Collazo, R.; De Santi, C.; Einfeldt, S.; Funato, M.; Glaab, J.; Hagedorn, S.; Hirano, A.; Hirayama, H.; Ishii, R.; Kashima, Y.; Kawakami, Y.; Kirste, R.; Kneissl, M.; Martin, R.; Mehnke, F.; Meneghini, M.; Ougazzaden, A.; Parbrook, P. J.; Rajan, S.; Reddy, P.; Römer, F.; Ruschel, J.; Sarkar, B.; Scholz, F.; Schowalter, L. J.; Shields, P.; Sitar, Z.; Sulmoni, L.; Wang, T.; Wernicke, T.; Weyers, M.; Witzigmann, B.; Wu, Y. R.; Wunderer, T.; Zhang, Y. The 2020 UV Emitter Roadmap. *J. Phys. D: Appl. Phys.* **2020**, *53* (50), 503001.

(5) Khan, A.; Balakrishnan, K.; Katona, T. Ultraviolet Light-Emitting Diodes Based on Group Three Nitrides. *Nat. Photonics* **2008**, *2* (2), 77−84.

(6) Kneissl, M.; Seong, T. Y.; Han, J.; Amano, H. The Emergence and Prospects of Deep-Ultraviolet Light-Emitting Diode Technologies. *Nat. Photonics* **2019**, *13* (4), 233−244.

(7) Brune, D.; Hellborg, R.; Persson, B.; Pääkkönen, R. Visible Light and UV Radiation. In *Radiation at home, outdoors and in the work place*; Scandinavian Science Publisher: 2001; p 69.

(8) Finlayson, L.; Barnard, I. R. M.; McMillan, L.; Ibbotson, S. H.; Brown, C. T. A.; Eadie, E.; Wood, K. Depth Penetration of Light into Skin as a Function of Wavelength from 200 to 1000 nm. *Photochem. Photobiol.* **2021**, DOI: 10.1111/php.13550.

(9) Downes, A.; Blunt, T. P. Researches on the Effect of Light upon Bacteria and Other Organisms. *Proc. R. Soc. London* **1878**, *26*, 488−500.

(10) Bedford, T. H. B. The Nature of the Action of Ultra-Violet Light on Micro-Organisms. *Br. J. Exp. Pathol.* **1927**, *8* (6), 437−441.

(11) Gates, F. L. A STUDY OF THE BACTERICIDAL ACTION OF ULTRA VIOLET LIGHT. *J. Gen. Physiol.* **1929**, *13* (2), 231−248.

(12) Fulton, H. R.; Coblentz, W. W. The Fungicidal Action of Ultra-Violet Radiation. *J. Agric. Res.* **1929**, *38* (3), 159.

(13) Kraissl, C. J.; Cimiotti, J. G.; Meleney, F. L. CONSIDERATIONS IN THE USE OF ULTRAVIOLET RADIATION IN OPERATING ROOMS. *Ann. Surg.* **1940**, *111* (2), 161−185.

(14) Overholt, R. H.; Betts, R. H. A COMPARATIVE REPORT ON INFECTION OF THORACOPLASTY WOUNDS: Experiences With Ultraviolet Irradiation of Operating Room Air. *J. Thorac. Surg.* **1940**, *9* (5), 520−529.

(15) HART, D.; SANGER, P. W. EFFECT ON WOUND HEALING OF BACTERICIDAL ULTRAVIOLET RADIATION FROM A SPECIAL UNIT: EXPERIMENTAL STUDY. *Arch. Surg.* **1939**, *38* (5), 797−805.

(16) ROBERTSON, E. C. AIR CONTAMINATION AND AIR STERILIZATION. *Arch. Pediatr. Adolesc. Med.* **1939**, *58* (5), 1023.

(17) Chinn, R. Y. W.; Sehulster, L. Guidelines for Environmental Infection Control in Health-Care Facilities; Recommendations of CDC and Healthcare Infection Control Practices Advisory Committee (HICPAC). *MMWR Recomm Rep.* **2003**, *52* (RR-10), 1−42.

(18) United Nations Environment Programme. Minamata Convention on Mercury, 2019; pp 1−72.

(19) Shatalov, M.; Jain, R.; Saxena, T.; Dobrinsky, A.; Shur, M. Development of Deep UV LEDs and Current Problems in Material and

Device Technology. In *Semiconductors and Semimetals*; Elsevier, Inc.: 2017; Vol. *96*, pp 45−83; DOI: 10.1016/bs.semsem.2016.08.002.
(20) Sharma, V. K.; Tan, S. T.; Haiyang, Z.; Shendre, S.; Baum, A.; Chalvet, F.; Tirén, J.; Demir, H. V. On-Chip Mercury-Free Deep-UV Light-Emitting Sources with Ultrahigh Germicidal Efficiency. *Adv. Opt. Mater.* **2021**, *9* (15), 2100072.
(21) Florez, D.; Diez, R.; Hay, K.; Piquet, H. DBD Excimer Lamp Power Supply with Fully Controlled Operating Conditions. *2012 13th International Conference on Optimization of Electrical and Electronic Equipment (OPTIM); IEEE* **2012**, 1346−1352.
(22) Wu, Y.; Yin, X.; Zhang, Q.; Wang, W.; Mu, X. The Recycling of Rare Earths from Waste Tricolor Phosphors in Fluorescent Lamps: A Review of Processes and Technologies. *Resour. Conserv. Recycl.* **2014**, *88* (100), 21−31.
(23) Bergman, R. S. Germicidal UV Sources and Systems. *Photochem. Photobiol.* **2021**, *97* (3), 466−470.
(24) Schalk, S.; Adam, V.; Arnold, E.; Brieden, K.; Voronov, A.; Witzke, H.-D. UV-Lamps for Disinfection and Advanced Oxidation - Lamp Types. *IVA News* **2005**, *8* (1), 32−37.
(25) Kogelschatz, U. Excimer Lamps: History, Discharge Physics, and Industrial Applications. In *Proc. SPIE*; Tarasenko, V. F., Ed.; SPIE: 2004; Vol. *5483*, pp 272−286; DOI: 10.1117/12.563006.
(26) Boyd, I. W.; Liaw, I. I. Development and Application of UV Excimer Lamps from 354nm −126nm. *High-Power Laser Ablation VI* **2006**, *6261* (June), 626104.
(27) Masoud, N. M.; Murnick, D. E. High Efficiency Fluorescent Excimer Lamps: An Alternative to Mercury Based UVC Lamps. *Rev. Sci. Instrum.* **2013**, *84* (12), 123108.
(28) Childress, J.; Roberts, J.; King, T. *Disinfection with Far-UV (222 nm Ultraviolet Light)*; Boeing: 2020; pp 1−6; https://www.boeing.com/confident-travel/research/CAP-3_Disinfection_with_Far-UV.html.
(29) Buonanno, M.; Welch, D.; Shuryak, I.; Brenner, D. J. Far-UVC Light (222 Nm) Efficiently and Safely Inactivates Airborne Human Coronaviruses. *Sci. Rep.* **2020**, *10* (1), 1−8.
(30) Barnard, I. R. M.; Eadie, E.; Wood, K. Further Evidence That Far-UVC for Disinfection Is Unlikely to Cause Erythema or Pre-Mutagenic DNA Lesions in Skin. *Photodermatol. Photoimmunol. Photomed.* **2020**, *36* (6), 476−477.
(31) Buonanno, M.; Ponnaiya, B.; Welch, D.; Stanislauskas, M.; Randers-Pehrson, G.; Smilenov, L.; Lowy, F. D.; Owens, D. M.; Brenner, D. J. Germicidal Efficacy and Mammalian Skin Safety of 222-nm UV Light. *Radiat. Res.* **2017**, *187* (4), 493−501.
(32) Yamano, N.; Kunisada, M.; Kaidzu, S.; Sugihara, K.; Nishiaki-Sawada, A.; Ohashi, H.; Yoshioka, A.; Igarashi, T.; Ohira, A.; Tanito, M.; Nishigori, C. Long-Term Effects of 222-Nm Ultraviolet Radiation C Sterilizing Lamps on Mice Susceptible to Ultraviolet Radiation. *Photochem. Photobiol.* **2020**, *96* (4), 853−862.
(33) Hirayama, H. *Growth Techniques of AlN/AlGaN and Development of High-Efficiency Deep-Ultraviolet Light-Emitting Diodes*; Kneissl, M., Rass, J., Eds.; Springer International Publishing: Cham, 2016; pp 75−113; DOI: 10.1007/978-3-319-24100-5_4.
(34) Shatalov, M.; Sun, W.; Lunev, A.; Hu, X.; Dobrinsky, A.; Bilenko, Y.; Yang, J.; Shur, M.; Gaska, R.; Moe, C.; Garrett, G.; Wraback, M. AlGaN Deep-Ultraviolet Light-Emitting Diodes with External Quantum Efficiency above 10%. *Appl. Phys. Express* **2012**, *5* (8), 082101.
(35) Adivarahan, V.; Wu, S.; Zhang, J. P.; Chitnis, A.; Shatalov, M.; Mandavilli, V.; Gaska, R.; Khan, M. A. High-Efficiency 269 Nm Emission Deep Ultraviolet Light-Emitting Diodes. *Appl. Phys. Lett.* **2004**, *84* (23), 4762−4764.
(36) Mino, T.; Hirayama, H.; Takano, T.; Noguchi, N.; Tsubaki, K. Highly-Uniform 260 Nm-Band AlGaN-Based Deep-Ultraviolet Light-Emitting Diodes Developed by 2-Inch × 3 MOVPE System. *Phys. status solidi* **2012**, *9* (3−4), 749−752.
(37) Hirayama, H.; Yatabe, T.; Noguchi, N.; Ohashi, T.; Kamata, N. 231−261 Nm AlGaN Deep-Ultraviolet Light-Emitting Diodes Fabricated on AlN Multilayer Buffers Grown by Ammonia Pulse-Flow Method on Sapphire. *Appl. Phys. Lett.* **2007**, *91* (7), 071901.
(38) Hirayama, H.; Yatabe, T.; Noguchi, N.; Kamata, N. Development of 230−270 Nm AlGaN-Based Deep-UV LEDs. *Electron. Commun. Japan* **2010**, *93* (3), 24−33.
(39) Hirano, A.; Nagasawa, Y.; Ippommatsu, M.; Aosaki, K.; Honda, Y.; Amano, H.; Akasaki, I. Development of AlGaN-Based Deep-Ultraviolet (DUV) LEDs Focusing on the Fluorine Resin Encapsulation and the Prospect of the Practical Applications. In *Proc. SPIE*; Lérondel, G., Kawata, S., Cho, Y.-H., Eds.; SPIE: 2016; Vol. *9926*, p 99260C; DOI: 10.1117/12.2235398.
(40) Maeda, N.; Hirayama, H. Realization of High-Efficiency Deep-UV LEDs Using Transparent p-AlGaN Contact Layer. *Phys. Status Solidi Curr. Top. Solid State Phys.* **2013**, *10* (11), 1521−1524.
(41) Chen, J.; Grandusky, J. R.; Moe, C. G.; Mendrick, M. C.; Jamil, M.; Gibb, S. R.; Schowalter, L. J. High Power Pseudomorphic Mid Ultraviolet Light Emitting Diodes with Improved Efficiency and Lifetime. In *Renewable Energy and the Environment*; OSA: Washington, DC, 2013; p DM2E.2; DOI: 10.1364/SOLED.2013.DM2E.2.
(42) Khan, A. AlInGaN-Based Deep Ultraviolet Light-Emitting Diodes and Their Applications Technology. *2013 Int. Conf. Compd. Semicond. Manuf. Technol. CS MANTECH 2013* **2013**, 41−44.
(43) Inoue, S. I.; Tamari, N.; Taniguchi, M. 150 MW Deep-Ultraviolet Light-Emitting Diodes with Large-Area AlN Nanophotonic Light-Extraction Structure Emitting at 265 nm. *Appl. Phys. Lett.* **2017**, *110* (14), 141106.
(44) Takano, T.; Mino, T.; Sakai, J.; Noguchi, N.; Tsubaki, K.; Hirayama, H. Deep-Ultraviolet Light-Emitting Diodes with External Quantum Efficiency Higher than 20% at 275 nm Achieved by Improving Light-Extraction Efficiency. *Appl. Phys. Express* **2017**, *10* (3), 031002.
(45) Hirayama, H.; Maeda, N.; Fujikawa, S.; Toyoda, S.; Kamata, N. Recent Progress and Future Prospects of AlGaN-Based High-Efficiency Deep-Ultraviolet Light-Emitting Diodes. *Jpn. J. Appl. Phys.* **2014**, *53* (10), 100209.
(46) Grandusky, J. R.; Chen, J.; Gibb, S. R.; Mendrick, M. C.; Moe, C. G.; Rodak, L.; Garrett, G. A.; Wraback, M.; Schowalter, L. J. 270 nm Pseudomorphic Ultraviolet Light-Emitting Diodes with over 60mW Continuous Wave Output Power. *Appl. Phys. Express* **2013**, *6* (3), 032101.
(47) Kinoshita, T.; Obata, T.; Nagashima, T.; Yanagi, H.; Moody, B.; Mita, S.; Inoue, S.; Kumagai, Y.; Koukitu, A.; Sitar, Z. Performance and Reliability of Deep-Ultraviolet Light-Emitting Diodes Fabricated on AlN Substrates Prepared by Hydride Vapor Phase Epitaxy. *Appl. Phys. Express* **2013**, *6* (9), No. 092103.
(48) Kinoshita, T.; Hironaka, K.; Obata, T.; Nagashima, T.; Dalmau, R.; Schlesser, R.; Moody, B.; Xie, J.; Inoue, S. I.; Kumagai, Y.; Koukitu, A.; Sitar, Z. Deep-Ultraviolet Light-Emitting Diodes Fabricated on Aln Substrates Prepared by Hydride Vapor Phase Epitaxy. *Appl. Phys. Express* **2012**, *5* (12), 122101.
(49) Pernot, C.; Kim, M.; Fukahori, S.; Inazu, T.; Fujita, T.; Nagasawa, Y.; Hirano, A.; Ippommatsu, M.; Iwaya, M.; Kamiyama, S.; Akasaki, I.; Amano, H. Improved Efficiency of 255−280 Nm AlGaN-Based Light-Emitting Diodes. *Appl. Phys. Express* **2010**, *3* (6), 061004.
(50) Fujioka, A.; Misaki, T.; Murayama, T.; Narukawa, Y.; Mukai, T. Improvement in Output Power of 280-Nm Deep Ultraviolet Light-Emitting Diode by Using AlGaN Multi Quantum Wells. *Appl. Phys. Express* **2010**, *3* (4), 041001.
(51) Adivarahan, V.; Sun, W. H.; Chitnis, A.; Shatalov, M.; Wu, S.; Maruska, H. P.; Khan, M. A. 250nmAlGaN Light-Emitting Diodes. *Appl. Phys. Lett.* **2004**, *85* (12), 2175−2177.
(52) Oto, T.; Banal, R. G.; Kataoka, K.; Funato, M.; Kawakami, Y. 100 MW Deep-Ultraviolet Emission from Aluminium-Nitride-Based Quantum Wells Pumped by an Electron Beam. *Nat. Photonics* **2010**, *4* (11), 767−771.
(53) Matsumoto, T.; Iwayama, S.; Saito, T.; Kawakami, Y.; Kubo, F.; Amano, H. Handheld Deep Ultraviolet Emission Device Based on Aluminum Nitride Quantum Wells and Graphene Nanoneedle Field Emitters. *Opt. Express* **2012**, *20* (22), 24320.

(54) Watanabe, K.; Taniguchi, T.; Niiyama, T.; Miya, K.; Taniguchi, M. Far-Ultraviolet Plane-Emission Handheld Device Based on Hexagonal Boron Nitride. *Nat. Photonics* **2009**, *3* (10), 591−594.
(55) Fukuyo, F.; Ochiai, S.; Miyake, H.; Hiramatsu, K.; Yoshida, H.; Kobayashi, Y. Growth and Characterization of AlGaN Multiple Quantum Wells for Electron-Beam Target for Deep-Ultraviolet Light Sources. *Jpn. J. Appl. Phys.* **2013**, *52* (1S), 01AF03.
(56) Ivanov, S. V.; Jmerik, V. N.; Nechaev, D. V.; Kozlovsky, V. I.; Tiberi, M. D. E-Beam Pumped Mid-UV Sources Based on MBE-Grown AlGaN MQW. *Phys. Status Solidi Appl. Mater. Sci.* **2015**, *212* (5), 1011−1016.
(57) Rong, X.; Wang, X.; Ivanov, S. V.; Jiang, X.; Chen, G.; Wang, P.; Wang, W.; He, C.; Wang, T.; Schulz, T.; Albrecht, M.; Jmerik, V. N.; Toropov, A. A.; Ratnikov, V. V.; Kozlovsky, V. I.; Martovitsky, V. P.; Jin, P.; Xu, F.; Yang, X.; Qin, Z.; Ge, W.; Shi, J.; Shen, B. High-Output-Power Ultraviolet Light Source from Quasi-2D GaN Quantum Structure. *Adv. Mater.* **2016**, *28* (36), 7978−7983.
(58) Tabataba-Vakili, F.; Wunderer, T.; Kneissl, M.; Yang, Z.; Teepe, M.; Batres, M.; Feneberg, M.; Vancil, B.; Johnson, N. M. Dominance of Radiative Recombination from Electron-Beam-Pumped Deep-UV AlGaN Multi-Quantum-Well Heterostructures. *Appl. Phys. Lett.* **2016**, *109* (18), 181105.
(59) Wang, Y.; Rong, X.; Ivanov, S.; Jmerik, V.; Chen, Z.; Wang, H.; Wang, T.; Wang, P.; Jin, P.; Chen, Y.; Kozlovsky, V.; Sviridov, D.; Zverev, M.; Zhdanova, E.; Gamov, N.; Studenov, V.; Miyake, H.; Li, H.; Guo, S.; Yang, X.; Xu, F.; Yu, T.; Qin, Z.; Ge, W.; Shen, B.; Wang, X. Deep Ultraviolet Light Source from Ultrathin GaN/AlN MQW Structures with Output Power Over 2 W. *Adv. Opt. Mater.* **2019**, *7* (10), 1801763.
(60) Jmerik, V. N.; Nechaev, D. V.; Toropov, A. A.; Evropeitsev, E. A.; Kozlovsky, V. I.; Martovitsky, V. P.; Rouvimov, S.; Ivanov, S. V. High-Efficiency Electron-Beam-Pumped Sub-240-Nm Ultraviolet Emitters Based on Ultra-Thin GaN/AlN Multiple Quantum Wells Grown by Plasma-Assisted Molecular-Beam Epitaxy on c-Al2O3. *Appl. Phys. Express* **2018**, *11* (9), 091003.
(61) Shimahara, Y.; Miyake, H.; Hiramatsu, K.; Fukuyo, F.; Okada, T.; Takaoka, H.; Yoshida, H. Fabrication of Deep-Ultraviolet-Light-Source Tube Using Si-Doped AlGaN. *Appl. Phys. Express* **2011**, *4* (4), 042103.
(62) Schubert, E. F.; Cho, J. Electron-Beam Excitation. *Nat. Photonics* **2010**, *4* (11), 735−736.

https://doi.org/10.1021/acsphotonics.2c00041
ACS Photonics 2022, 9, 1513−1521