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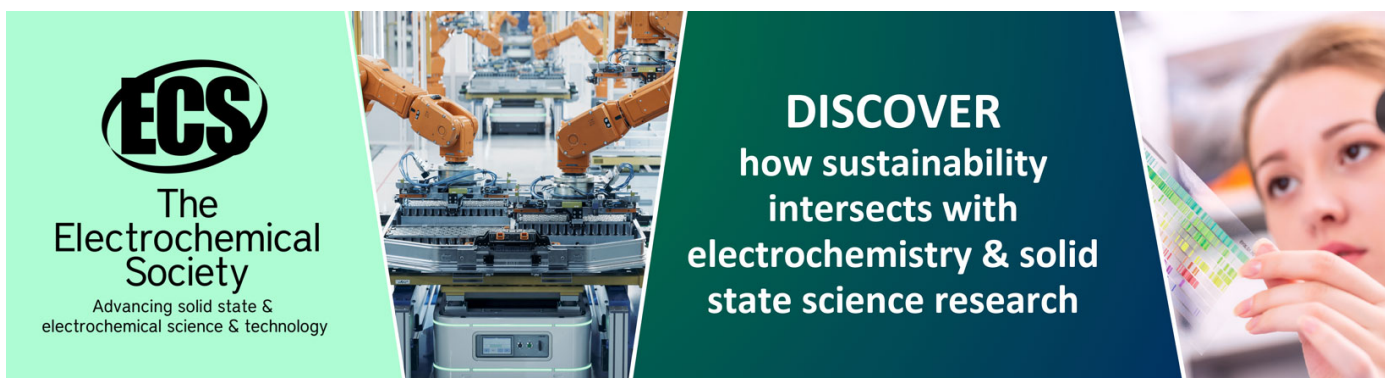
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Invited Article

Development and future of ultraviolet light-emitting diodes: UV-LED will replace the UV lamp

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Abstract

Ultraviolet light-emitting diodes (UV-LEDs) have started replacing UV lamps. The power per LED of high-power LED products has reached 12 W (14 A), which is 100 times the values observed ten years ago. In addition, the cost of these high-power LEDs has been decreasing. In this study, we attempt to understand the technologies and potential of UV-LEDs.

Keywords: ultraviolet light-emitting diodes, ultraviolet lamps, mercury, resin curing, exposure

(Some figures may appear in colour only in the online journal)

1. Introduction

We started the development of the world's first ultraviolet light-emitting diodes (UV-LEDs) in collaboration with the University of Tokushima in April 2000, and have been supplying related products ever since. In recent years, as people are becoming more concerned about protecting the environment, and in light of INC5, where it was made clear that production, use, and trade of mercury will be reduced, the role of UV-LEDs is becoming more important.

UV-LEDs are LEDs that emit UV rays with a wavelength of approximately 400 nm or shorter. They are divided into near-ultraviolet light-emitting diodes (NUV-LEDs), whose emission wavelength is approximately 300–400 nm, and deep-ultraviolet LEDs (DUV-LEDs), whose emission wavelength is approximately 200–300 nm. UV-LEDs are promising candidates for various applications: replacing UV lamps; fluorescence light sources for lighting and displays; high-resolution light sources for microscopes and exposure machines; light sources for chemical excitation as used for

resin curing, medicine, and biotechnology; excitation light sources for spectroscopy as used for banknote identification, DNA chips, and environmental monitoring; sanitary light sources for disinfection and sterilization (figure 1).

UV-LEDs that emit light at a power of a few milliwatts have already replaced UV lamps for banknote identification in automated teller machines. Prototype light sources for resin curing and exposure machines (which require a large cumulative light intensity) have been made, and commercial products are being released accordingly. The external quantum efficiency of NUV-LED, in particular, has greatly improved because of developments in crystal growth, chip processing, and packaging technologies, reaching 30% at a wavelength of 365 nm, 50% at 385 nm, and 60% at 405 nm (our product). The power per LED of high-power products at a wavelength of 365 nm has reached 12 W (14 A) (figure 2), which is 100 times the values from ten years ago, 118 mW (500 mA) [1]. The cost of these high-power LEDs has decreased as a result of mass production, making them available for various applications.

In comparison to UV lamps, UV-LEDs are not only mercury free, but also have (1) a higher energy efficiency, (2) a longer lifetime, (3) more constant light intensity, and (4) it is easy to control their temperature and heat (figure 3). For all these reasons, UV-LEDs are expected to be more widely used



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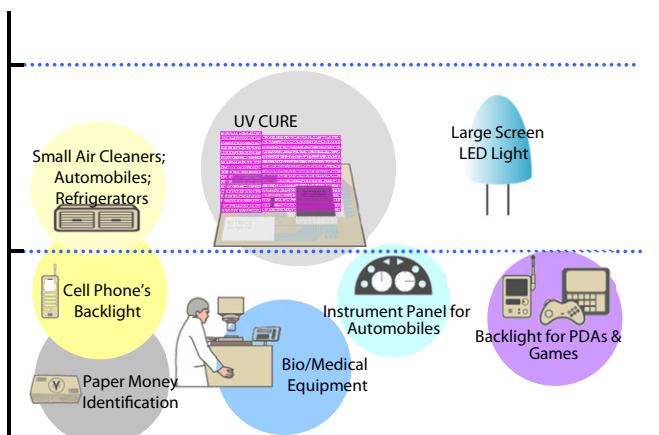


Figure 1. UV LED application market.

in the future [2]. Moreover, since the current mainstream white LEDs, which use blue LEDs and yellow phosphors, are not very good at color rendering, UV-red, green, and blue (RGB) white LEDs (which produce white light by exciting phosphors of the three RGB colors with UV) are highly anticipated as a next-generation lighting device [3].

In this study, we will discuss the development process and future of UV-LEDs in the NUV range.

2. Problems to improve the performance of UV-LEDs

GaN LEDs (including UV-LEDs) are fabricated by depositing GaN crystal layers onto the C-plane of sapphire (Al_2O_3) using the metalorganic chemical vapour deposition (MOCVD) method. It is not an overstatement to say that the history of GaN LED development has been a battle against the sapphire on which the layers are deposited. That is, it is difficult to grow high-quality crystalline layers because the lattice constants for sapphire and GaN are different. Moreover, while the melting point of sapphire is over 2000 °C, making it suitable for epitaxial growth at high temperatures over 1000 °C, sapphire has a high Vickers hardness of approximately 20 GPa, making it difficult to process the wafer. Sapphire also retains heat, with a thermal conductivity of 40 W mK⁻¹; therefore, it is not effective at dissipating heat. Furthermore, since sapphire is an insulator, the electrostatic breakdown voltage of the light-emitting layer is low, and the *n*-electrode cannot be located on

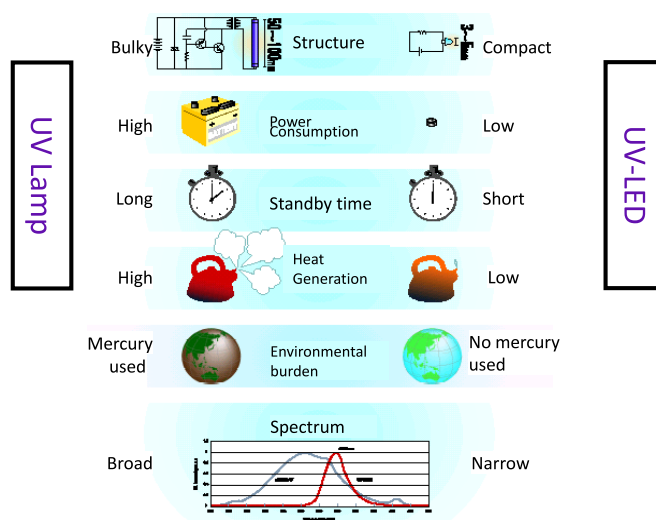


Figure 3. Features of UV-LED against UV lamp.

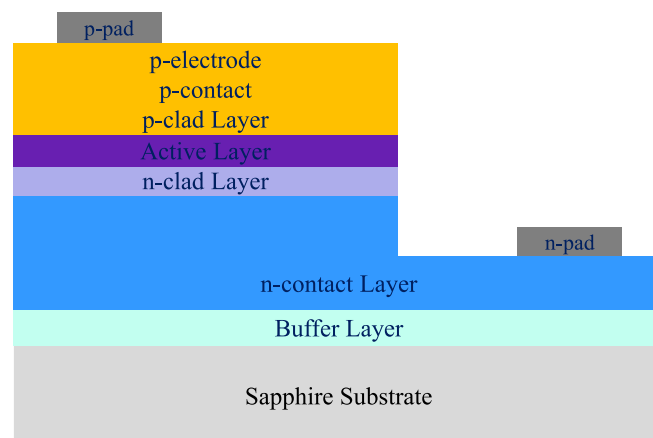


Figure 4. Structural diagram of a common UV-LED chip.

the other side of the sapphire substrate. This indicates that the vertical chip (V chip) structure cannot be employed, resulting in a smaller light-emitting area.

Figure 4 shows the typical structure of a face-up UV-LED chip. A short wavelength (wide band gap) is required for the light-emitting layer. The shortest wavelength achievable using the InGaN series of materials corresponds to 3.4 eV (the band gap of GaN). To further shorten the wavelength, materials from the $\text{Al}_x\text{In}_y\text{Ga}_{1-x-y}\text{N}$ series can be used, for example, AlN

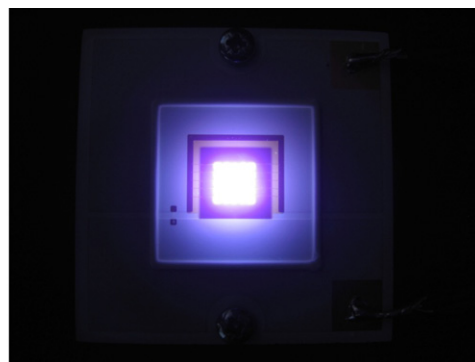
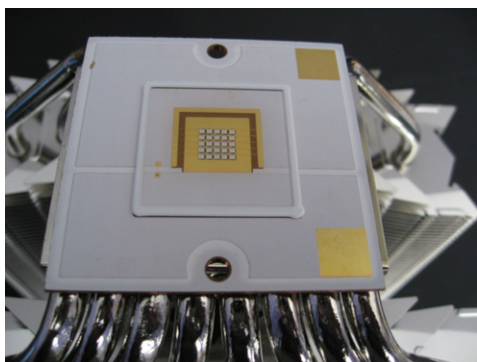


Figure 2. High power UV-LED module wavelength 365 nm 12 W(14 A) Wavelength 385 nm 17 W(14 A).

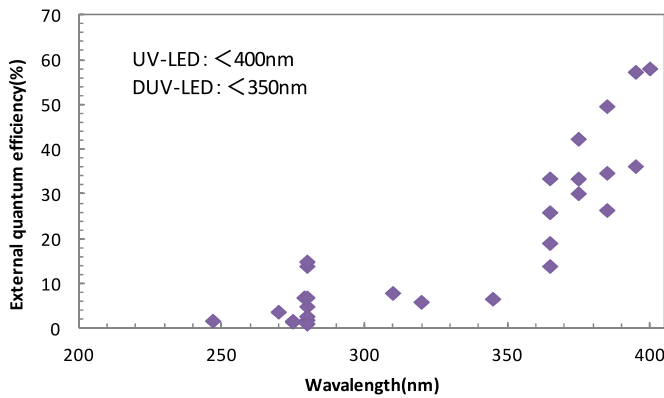


Figure 5. External quantum efficiency of UV-LEDs and DUV-LEDs.

with a band gap of 6.2 eV. The crystal growth process is as follows. Since the lattice constants for the sapphire substrate and GaN are different, a GaN buffer layer is used to form an *n*-GaN contact layer. On top of the *n*-contact layer, an $\text{Al}_x\text{In}_y\text{Ga}_{1-x-y}\text{N}$ light-emitting layer is sandwiched between AlGaIn barrier layers, forming a double heterostructure. Then, a *p*-GaN contact layer is formed on top of the heterostructure, and transparent electrodes are finally formed on top. As shown in figure 4, the *n*-electrode must be formed by etching the light-emitting surface. This step not only reduces the light-emitting area, but the wires required for bonding also hinder light emission.

Due to the different lattice constants of the sapphire substrate and GaN, the crystals will have a dislocation density of $5\text{--}50 \times 10^8 \text{ cm}^{-2}$. It is thought that the high light-emitting efficiency of a blue (InGaIn) LED, despite the high dislocation density, is because of non-uniformities in the In concentration. To shorten the wavelength, the In concentration must be reduced, indicating that any effect from the variations in In composition will be reduced [4].

Figure 5 shows published values of the external quantum efficiency for UV-LEDs and DUV-LEDs [5–11], which decrease with wavelength. Three possible causes for this decrease in efficiency, all related to crystal growth, are as follows.

- (1) A decrease in light-emitting efficiency due to a high dislocation density in the active layer.

The crystals in InGaIn LEDs have a high dislocation density; however, in the case of UV-LEDs, the active layer is AlGaIn, which requires a cladding layer with an even larger band gap, resulting in an even higher threading dislocation density.

- (2) A decrease in the effect of the variations in In composition due to a decrease in the In composition in the active layer.

To shorten the emitted wavelength of the LED, the In composition must be decreased, and accordingly, the effect of any variations in the composition is reduced. When there is a high In composition, electrons and holes rapidly recombine (before getting captured by a dislocation); however, as the In composition decreases, the charges interact more with dislocations.

- (3) A decrease in the light-extraction efficiency due to UV absorption by the GaN buffer layer.

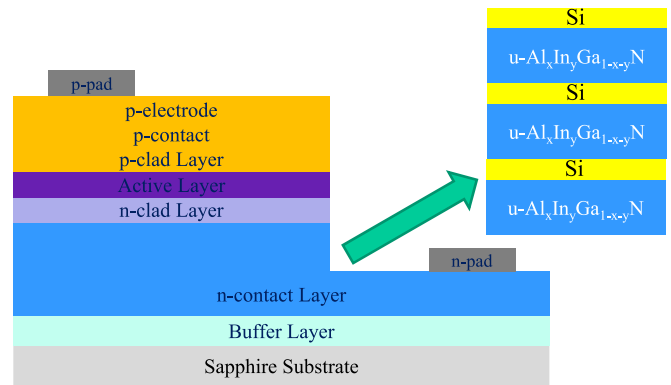


Figure 6. Schematic of Si layers and undoped AlInGaIn layers.

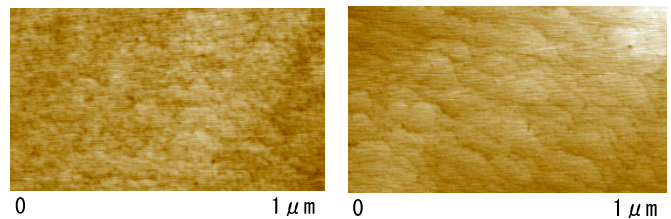


Figure 7. Surface AFM images (left: *n*-GaN single layer, right: undoped AlInGaIn layer).

In UV-LEDs emitting a wavelength of 365 nm, UV radiation of $\leq 370 \text{ nm}$ is absorbed by the GaN buffer layer growing on the sapphire substrate as a base (the band gap energy of GaN is 3.4 eV), resulting in a rapid decrease in the light-extraction efficiency. This problem can be solved by using AlGaIn as the buffer layer. However, this would increase the Al composition and in turn decrease the crystallinity. Also, deepening of the Mg acceptor level would make it difficult to make the AlGaIn layer *p*-type, and the larger difference in lattice constants would cause cracking in the films.

Therefore, the following three points are considered important for increasing the efficiency and power of UV-LEDs: (1) decreasing the dislocation density; (2) increasing the variation in In composition; (3) decreasing UV absorption by the GaN buffer layer.

3. Increasing the efficiency and power of UV-LEDs

The problems regarding the development of UV-LEDs were discussed in the previous chapter; here we will elaborate on how to handle these.

- (1) Decreasing the dislocation density.

To reduce crystal defects, we have found a method for alternately depositing Si and undoped AlInGaIn layers during the formation of the *n*-contact layer (figure 6). Figure 7 shows surface AFM images of such a sample. The stepped surface can be seen more clearly compared to when a Si-doped single *n*-GaN/AlGaIn layer is used as the *n*-contact layer, and smoother ridges are formed. This is probably due to the diffusion effect of Si that helps secure carriers in the *n*-contact layer while improving the crystallinity. In addition, with In being captured by defects, the crystal defects are reduced even further [12].

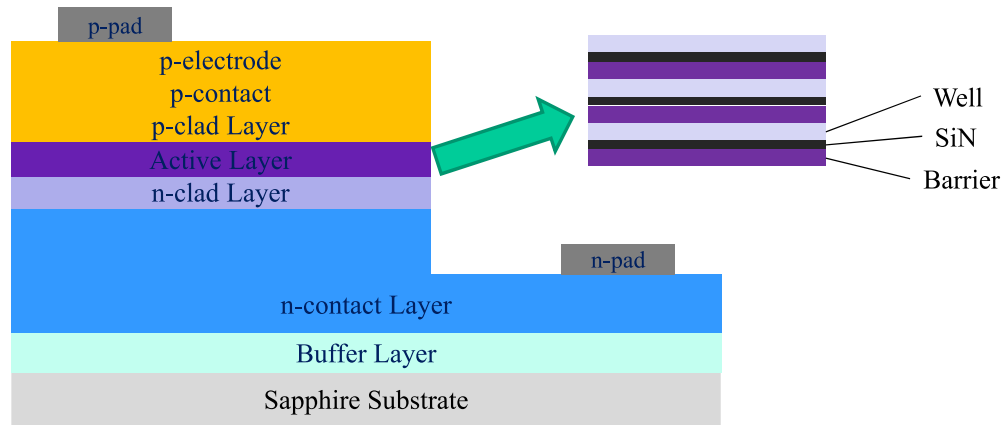


Figure 8. Structural diagram of UV-LED with SiN layer inserted.

We also observed that the dislocation density could be reduced by 30–50% compared to the conventional structure using a low-temperature SiN buffer layer [13, 14], a high-temperature SiN intermediate layer [15], and a low-temperature GaNP buffer layer [16]. All of these methods are highly effective because they can reduce the dislocation density without complex processing.

There are also epitaxial lateral overgrowth (ELO) techniques that promote growth in the lateral directions using striped sapphire. Khan *et al* of the University of South Carolina succeeded in obtaining a thick AlGaIn layer with a dislocation density of 10^8 cm^{-2} (which is close to the proposed ideal value of 10^7 cm^{-2}) by growing an AlGaIn layer on a sapphire substrate and an AlN buffer layer, patterning the AlGaIn layer with stripes using lithography and reactive ion etching, and continuing to grow the AlGaIn layer on top with ELO [17].

Using a patterned sapphire substrate (PSS), growth in the lateral directions can be promoted; thus, the ELO can reduce dislocations [18].

(2) Increasing the variation in In composition.

We have examined a method to promote the variation in the In composition, and in collaboration with the University of Tokushima, we proposed a method of using a SiN layer or a Ga droplet layer in the active layer. Figure 8 shows the structure of a UV-LED where an SiN layer is inserted into the active layer. By depositing a monolayer of SiN, crystals at its base become partly exposed, forming nanosized holes. If an AlInGaIn layer is deposited over it, regions with different compositions will be created because Ga, In, and Al atoms adsorb to different degrees. While Al atoms are not easily transported on the SiN layer, Ga and In atoms are transported easily. This causes formation of a structure with nanoscale compositional differences, and In-rich regions can be created (figure 9) [19, 20].

(3) Decreasing UV absorption by the GaN buffer layer.

Techniques to increase the light-extraction efficiency and those used during the processing of InGaIn LEDs are basically the same.

Figure 10 lists some of these techniques. The numbers show the output ratio of a face-up chip with a wavelength

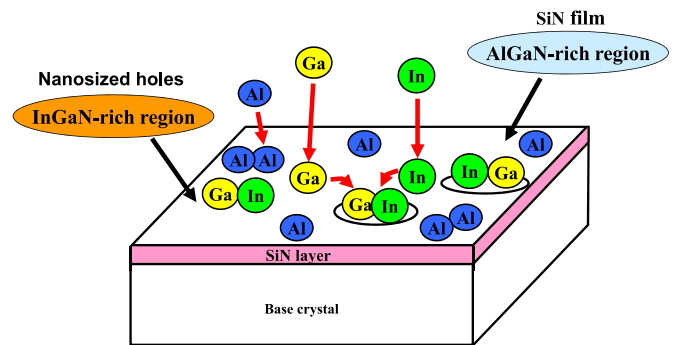


Figure 9. Model of non-uniform In composition created by adding SiN.

of 375 nm and the numbers in parentheses show at a wavelength of 365 nm. This value can reach up to 4 for these processes, and more than 7 at a wavelength of 365 nm.

Here we briefly explain each process of development. First, face-up chips are easy to process and their production costs are low; therefore, they are still widely used for mass-produced InGaIn LEDs. Note that the progression of surface processing technology has led to outputs up to 2.5 times greater than the most basic chips. This is a result of the increased refractive index due to processing on the front and back surfaces of the sapphire substrate, *p*-layer surface, and transparent electrode surface [21]. For the *p*-type transparent electrode, indium tin oxide, which absorbs less UV light than conventional Ni/Au, is used.

Table 1 shows the results of analyzing three different patterns of PSS substrates at a wavelength of 375 nm. Shape No. 4 showed the best result, increasing the output with a high and narrow-pitched PSS. However, if the cones are high and the pitch is narrow, it is difficult to form an epitaxial film; the pattern must allow both a reduction in the amount of dislocations (from the epitaxial layer) and an increase in the light-extraction efficiency (from the increased refractive index). Figure 11 shows the output of our dome-shaped plastic UV-LED products over time. In 2009 we commercialized a dome-shaped plastic LED (figure 12) with a world-leading efficiency: an output

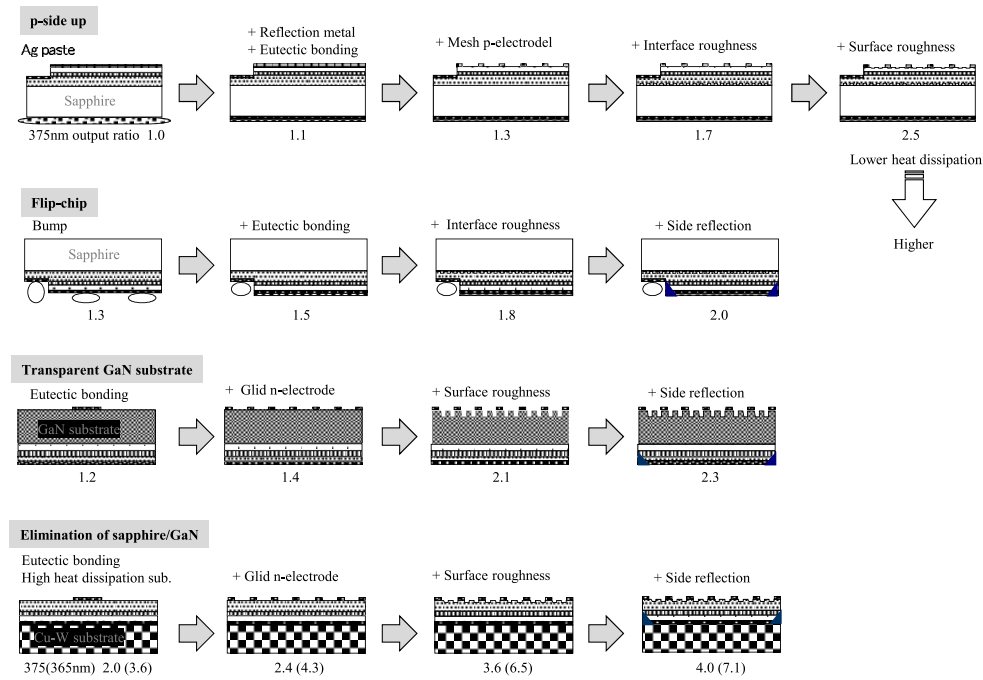


Figure 10. LED chip process method.

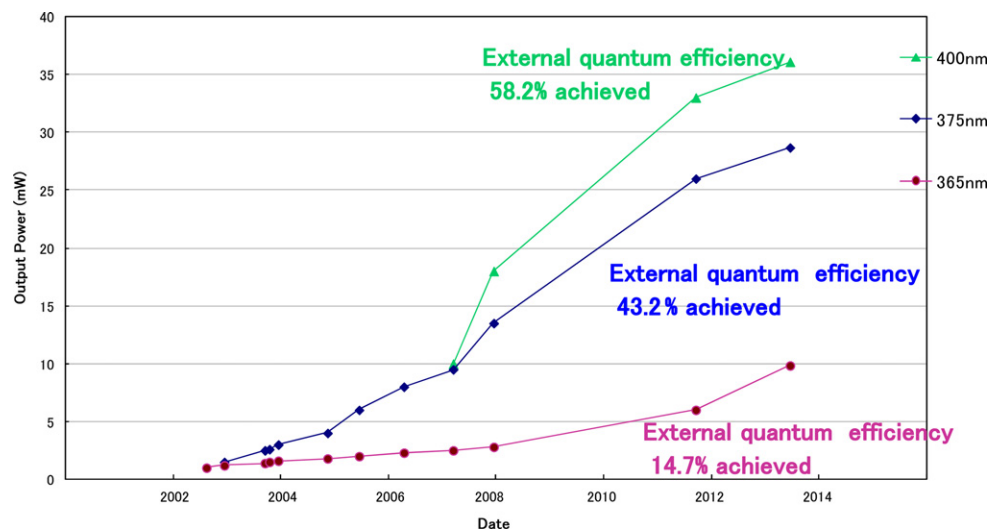


Figure 11. External quantum efficiency over time of our dome-shaped plastic UV-LED products.

Table 1. Results of PSS shape examination.

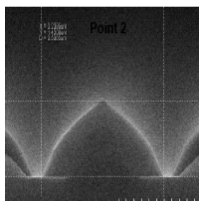
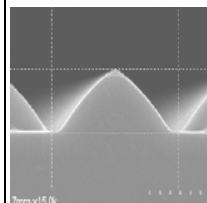
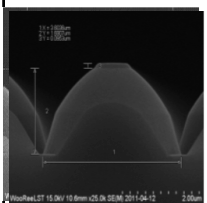
		No.1		No.2		No.3		No.4	
SEM		non-PSS							
Pith [μm]		-		0.78		0.541		0.405	
Height [μm]		-		1.42		1.435		1.72	
		[nm]	[a.u.]	[nm]	[a.u.]	[nm]	[a.u.]	[nm]	[a.u.]
Wavelength	Intensity	375.05	2.86	375.31	3.65	375.82	3.80	374.51	3.86



Figure 12. Dome-shaped UV-LED ‘NS375L-ERLM’.

of 28.7 mW (20 mA, external quantum efficiency of 43.2%) at a wavelength of 375 nm, and an output of 36.1 mW (20 mA, external quantum efficiency of 58.2%) at a wavelength of 400 nm. Next, flip chip is a technology that produces red III–V LEDs that perform well both in heat radiation and light-extraction efficiency [22]; however, for InGaN LEDs, it does not produce devices that performed as well as expected, because of the light transmission rate and refractive index of the sapphire substrate.

As for the reduction in dislocations using a GaN substrate, a bulk substrate is used to avoid the lattice mismatch with sapphire. However, our results were not as good as those of other research teams [23] using the InGaN series. It appears that the effect of dislocations was large because the dislocation of the GaN substrate was still as large as $5 \times 10^6 \text{ cm}^{-2}$, and the effect of the variation in the In composition was small for the AlInGaN series.

Finally, we discuss here the removal of sapphire/GaN layers. This method is the most effective and a high-level

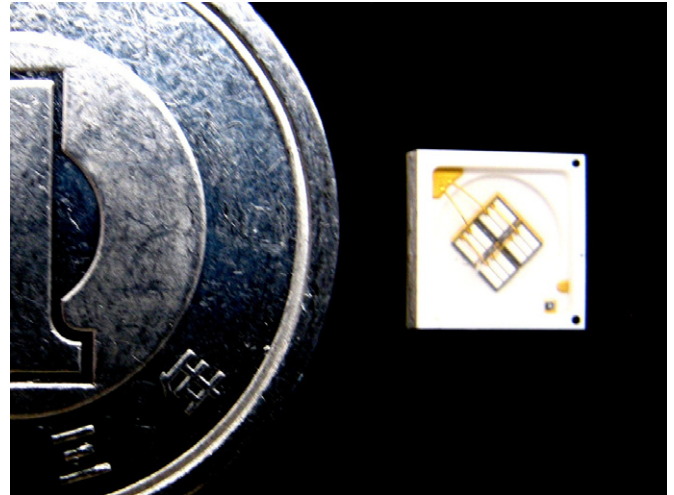


Figure 14. High-power UV-LED wavelength: 365 nm output power: 2110 mW(2 A) wavelength:385 nm output power:3210 mW(2 A).

processing technique in which an LED structure is built on a sapphire substrate, and then the *p*-side is attached to a thermally conductive metal such as CuW, and finally, the sapphire substrate and the UV absorption layer are lifted off. Two of the lift-off methods are laser lift off [24, 25] (using an excimer laser) and chemical lift off [26] (using an etching process). A chip that has *p*- and *n*-electrodes on the top and bottom in this manner is called a V chip (figure 13) [27–29]. In April 2013, we examined crystal structures suited for V chips, and obtained the following results with a surface-mounted device LED (figure 2): output of 2110 mW (2 A, external quantum efficiency of 31.1%) at a wavelength of 365 nm, and an output of 3210 mW (2 A, external quantum efficiency of 49.8%) at a wavelength of 385 nm (figure 14).

We have succeeded in obtaining an output of 12 W(14 A) at a wavelength of 365 nm and 17 W (14 A) at a wavelength of 385 nm by the 25 pcs V chip mounted module on the 50 mm square copper substrate in February 2014 (figure 2).

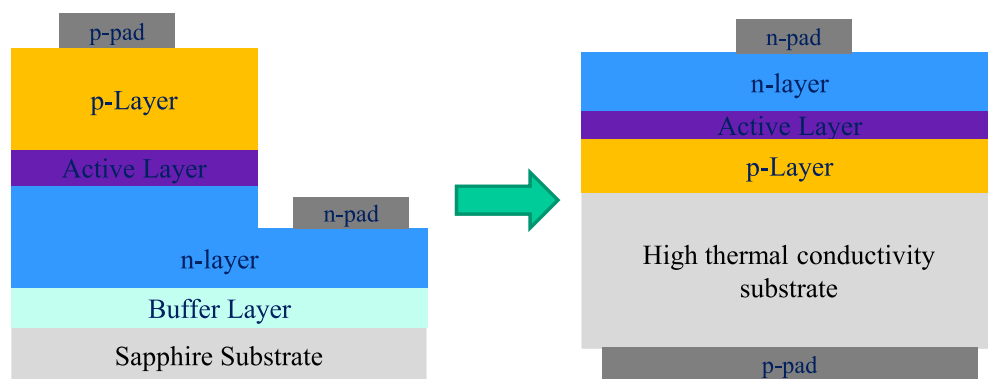


Figure 13. LED structure diagram (left: face-up LED, right: V chip LED).

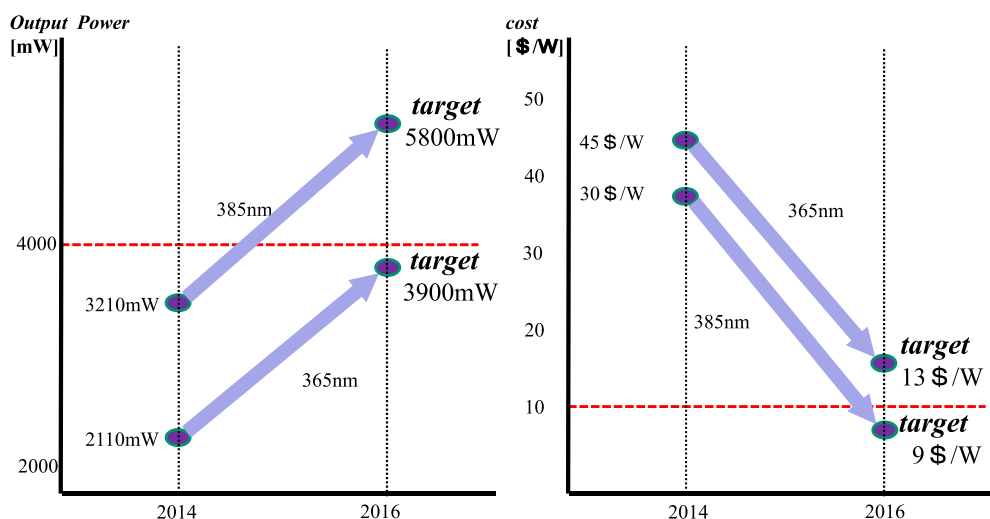


Figure 15. Prediction of output power and cost.

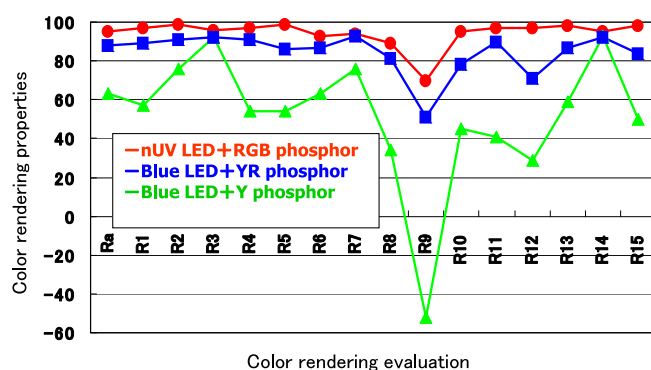


Figure 16. Comparison of color rendering properties of warm white LEDs.

4. Conclusions

In this study, we briefly explained the flow of the technological development to increase the power and efficiency of NUV-LEDs. The intensity of $1\text{--}10\text{ W cm}^{-2}$, which is required for applications involving large cumulative light intensity such as light resin curing, has already been achieved, and the production costs were also dramatically decreased because of an increase in the diameter of MOCVD reactors. The wafer size is also increasing from the conventional 2 inches to 4, 6, and 8 inches; therefore, it is possible to decrease the costs. Figure 15 shows a prediction of an output and a cost over time in the future. Current problems such as deterioration of die adhesive, sealing resin and packaging from UV rays, and a decrease in the reflection rate of reflectors such as gold/silver coatings are being overcome by improvements in materials technology. In the future, to meet the demands for substituting UV lamps, in addition to increasing the power and efficiency, analyzing the reaction mechanism of each application will be important. For example, in the case of resin curing, since the emission spectra of UV-LEDs are very narrow compared to mercury lamps, it has been observed that with a single wavelength, e.g. 365 nm, the wavelength component necessary to initiate the chemical reaction was not present. White LEDs made of



Figure 17. White LED made of NUV + RGB phosphors.

400 nm NUV-LEDs and RGB phosphors, when used as the backlight for LCD TVs, showed a high colour reproducibility of over 100% for NTSC, and when used as white light, they showed a high colour rendering index of Ra95 or higher (figures 16 and 17) [2]. Although a sterilization effect has not been observed at NUV wavelengths, NUV-LEDs have been applied to home appliances such as air conditioners and

refrigerators in combination with photocatalysts. In the future, the choice of wavelengths and illumination methods need to be optimized according to the application.

We will continue our technological study to further increase the power and efficiency, and accelerate the development of applications in the hope that we can contribute to improvements in the global environment through energy savings and a mercury-free society where people can live fulfilled lives.

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