Deep Ultraviolet Light Emitting Diode Based on Aluminum Gallium Nitride

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Abstract. AlGaN-based deep ultraviolet LED has gradually attracted people's attention, because it can be used in sterilization, secret communication and other fields. According to the research report of nearly twenty years, there are still many shortcomings in the external quantum efficiency, internal quantum efficiency and light extraction efficiency of AlGaN-based deep ultraviolet LED. For this reason, researchers have made many efforts at the chip level, including epitaxial and doping technology. In recent years, more and more researchers have studied packaging technology with low light efficiency caused by Fresnel and total reflection. In epitaxial technology, this paper mainly introduces the material selection of substrate and the use of buffer layer. In this paper, the most commonly used substrate selection and the existing problems and solutions of substrates are summarized. The current process of buffer layer is also introduced. On the doping level, the present situation and development of N-type doping and P-type doping are introduced respectively. The use of the latest doping elements is introduced in this paper. Packaging technology explains the choice between organic materials and inorganic materials, and how the packaging structure can avoid the reflection loss of light to the maximum extent. Finally, the article predicts the future development direction.

Keywords: AlGaN, Deep ultraviolet, LED, Packaging.

1. Introduction

Deep ultraviolet LED technology has made rapid development in recent years, on the one hand, it benefits from the progress of nitride material epitaxy and doping technology in the chip manufacturing process, on the other hand, it is the development of deep UV LED packaging technology.

Deep ultraviolet LED is an LED whose light emission wavelength is below medium ultraviolet. That is, those with wavelengths below 320 nanometers [1].In recent years, deep ultraviolet light-emitting diodes have great development potential and application market in the fields of air and water purification, biomedical inspection, illumination, sterilization and disinfection because of their advantages of environmental protection, small size, long service life and adjustable luminous wavelength [2].Although deep ultraviolet LED has many advantages, compared with near ultraviolet or blue LED, its cost is extremely high, and its light efficiency and reliability are low, which is far from meeting the application requirements [3].

In the past twenty years, researchers have tried improving EQE and WPE by improving the quality of epitaxial crystals and reducing the interface reflection loss. However, when the emission wavelength is shorter than 365nm, the EQE is usually lower than 10% in the range containing deep ultraviolet LED. The main causes of this phenomenon are low doping of N or P type, strong UV absorption materials, poor LEE, and low-quality epitaxial crystals. So far, the highest EQE obtained is 20.3% made by Gaoye Group in 2017. There is still a lot of room for improvement. WPE is mostly below 10%. So the required driving voltage is larger now. The main influencing factors of LEE are Fresnel loss, total internal reflection (TIR) loss and ultraviolet absorption of packaging materials. Therefore, research on deep ultraviolet LED needs to make efforts on chip and packaging technology around those several efficiencies [4].

This paper will summarize the development of deep ultraviolet LED on chip and package level, and the future research direction will be analyzed.

2. Basic properties of AlGaN materials

The ternary alloy AlGaN, which consists of GaN and AlN, has an extremely large band gap. Adjusting the Al composition can continuously change the band gap from 3.4eV to 6.2eV. Its corresponding wavelength covers the wide band gap spectrum from UVA to UVC, so LED devices with full ultraviolet range can be manufactured [1] [3].

Crystal structure and electron configuration jointly determine the energy band structure of materials. AlGaN shares a crystal structure similar to GaN and AlN, wherein the wurtzite structure is most stable at room temperature and atmospheric pressure. The wurtzite structure belongs to the hexagonal system, with hexagonally closely packed metal atoms and nitrogen atoms nested within. It possesses two independent lattice constants, denoted as "a" and "c," with an ideal lattice constant ratio of 1.633. The lattice constant ratio of AlGaN is less than 1.633 and can be calculated using the Vegard formula [5]:

$$(AlxGa1{-}xN) = x \cdot a\,(AlN) + (1-x) \cdot a\,(GaN) \quad (1)$$

$$(AlxGa1{-}xN) = x \cdot c\,(AlN) + (1-x) \cdot c\,(GaN) \quad (2)$$

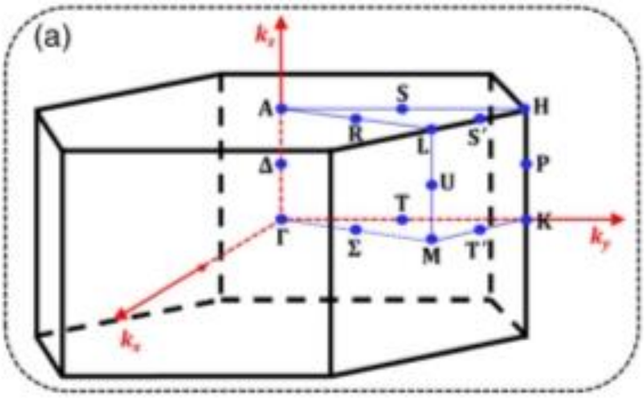

Figure 1. First Brillouin zone in reciprocal space for the WZ AlGaN structure [5].

As seen in Figure 1, the greatest energy of the valence band and the minimum energy of the conduction band of the AlGaN semiconductor material with direct band gap are at the center point of the first Brillouin zone in the reciprocal space of the wurtzite structure. Kx, Ky, and Kz are orthogonal to each other. The formula that uses the Al component as a variable can be used to determine the band gap width [6]:

$$E\,(AlxGa1{-}xN) = x \cdot Eg\,(AlN) + (1-x) \cdot Eg\,(GaN) - bx\,(1-x) \quad (3)$$

Its energy band structure determines its excellent optoelectronic properties. AlGaN offers several advantages as a UV light source, including compact volume, high efficiency, low working voltage, long service life, and environmental protection without any hazardous materials. [1].

3. AlGaN-based DUV LED technology

Since the development of deep ultraviolet LED for more than 20 years, although researchers have made a lot of efforts and made a lot of progress, with the light-emitting wavelength of deep ultraviolet LED gradually becoming shorter, the epitaxy, doping technology and packaging technology of high-quality AlGaN materials are still facing challenges. Whether it is light efficiency or quantum efficiency, there is much room for improvement of AlGaN-based deep ultraviolet LED in various efficiencies. The following will focus on several key indicators, such as IQE, EQE, LEE, and discuss the efforts and development status of material epitaxy, doping technology and packaging technology, respectively, and evaluate and compare to analyze the next development direction [4].

For a better understanding, there are key indicators to judge the performance of deep ultraviolet LEDs.

Internal quantum efficiency (IQE) is the first. It can be defined numerically as the ratio of photons produced to carriers supplied in a given time interval.

The ratio of photons emitted per second to carriers injected per second is known as external quantum efficiency, or EQE. EQE is a key point that needs to be improved. As shown in figure 2, the external quantum efficiency of InGaN-based near-ultraviolet LED with wavelength above 365nm has reached 76% at the highest. At the same time, that of AlGaN-based deep-ultraviolet LED is generally less than 20%, among which the external quantum efficiency of 265-280nm is less than 5% for sterilization and disinfection. The primary causes of this are low doping of N-type and P-type, high UV absorption materials, poor LEE, and low-quality epitaxial crystals.

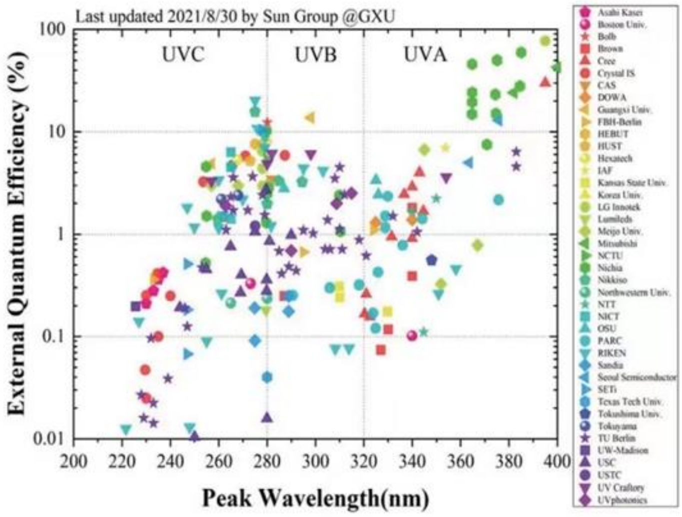

Figure 2. EQE at different peak wavelengths [4].

Light extraction efficiency (LEE) is the ratio of the number of photons emitted per second to the number of photons generated per second, which is EQE/IQE [4].

3.1. Epitaxial technology

The typical epitaxial structures of AlGaN-based DUV LED are substrate, AlN buffer layer or template, AlN or AlGaN superlattice, AlGaN type layer, multi-quantum well, AlGaN p type layer and GaN p type ohmic contact layer. Sapphire substrate is commonly used for the substrate. It is transparent to ultraviolet light in the required range, and is cheap and easily available, so it is widely used. However, it has lattice mismatch and thermal mismatch with AlGaN material, and has poor thermal conductivity and insulation. SiC substrate has little lattice mismatch and good electrical and thermal conductivity. People have done a lot of research on this basis. Nishida group, for example, first achieved luminescence with a wavelength of 346nm on the SiC substrate, and then applied the short-period alloy superlattice structure to the SiC substrate, effectively improving the electrical properties of the device, achieving a luminescence wavelength of 350mm and a maximum output power of 0.1mW. Later, they used a single quantum well structure to realize the UV LED with the emission wavelength of 341-343nm, and the optical output power exceeded 1mW [7]. In 2012, kinoshita et al. fabricated AlGaN-based DUV LED on AIN substrate with hydride vapor phase epitaxy, which improved the output power to some extent [8]. Although Si substrate has also been attempted, it remains challenging due to the blatant lattice mismatch and thermal mismatch with AlGaN epitaxial materials [7].

Low-temperature AlN or GaN buffer layers are utilized as the initial nucleation layer to lower the dislocation density of epitaxial materials since sapphire substrates are the most commonly used. For the conventional low-temperature buffer layer, the epitaxial layer's crystal quality can be enhanced, but the impact on the sapphire substrate is unfavorable. This process greatly influences the threading dislocation density (TDD) in AlGaN materials. The high level of TDD will seriously affect the device performance of DUV LED. To solve this problem, Hamamatsu Photonics Co., Ltd. of Japan adopted a lateral epitaxial technique controlled by heterogeneous crystal planes to prepare SiO2 stripe mask on the GaN template, and obtained a crack-free epitaxial layer of 30%Al composition. Using low-pressure metal organic chemical vapor deposition, Hideki Hirayama and colleagues developed the ammonia pulse flow multi-layer growth process in 2014. This increased the emission intensity by around 80 times compared to the conventional method and enhanced the IQE [7] [9].

3.2. Doping technology

The most prevalent N-type and P-type doping components for AlGaN materials are Si and Mg, respectively. N-type doping is progressing well at present. As early as 2002, when the Al content reached 80%, the electron concentration was still 0.85× 10^19 cm^-3, but the electron mobility was low. The AlGaN material with an 85% Al component, 0.1Ω cm resistivity, 6× 10^18 cm^-3 doping concentration, 1× 10^18 cm^-3 carrier concentration, and more than 40 cm^2 V^-1 s^-1 carrier mobility was designed by Collazo and his colleagues in 2011. This material can provide N-type conductivity for DUV LEDs with a wavelength of 250–260 nm [7].

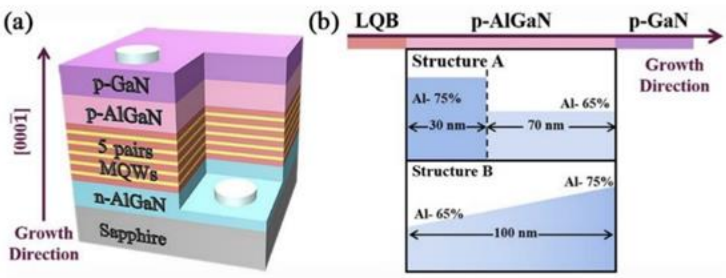

Figure 3. (a) Nitrogen polarity LED device structure
(b) p-AlGaN structure in LED devices A and B [9].

One of the main issues has always been P-type doping efficiency. A schematic illustration of P doping is shown in Figure 3. International research has been done on Mg doping, superlattice doping, co-doping, and polarization-induced doping in relation to P-type doping. The main problem is the low hole concentration. In particular, the hole concentration can be as low as 10^{14} cm $^{-3}$ when the Al content exceeds 60%. Deep UV LED's electron injection efficiency is decreased as a result of electron leakage to the P layer. p-GaN contact layer is the only one that many researchers can use. But this makes LEE significantly lower. Because of the low LEE, the electron injection efficiency is reduced. 2014 Japanese researchers designed and used highly reflective Ni (1nm)/Ai (150nm). A very thin Ni layer (less than 1 nm) was inserted between the Al layer and the p-AlGaN layer to raise the reflectivity of the P-type electrode from 30% to 64%. They improved LEE and got the maximum EQE of 3.1% and 2.8%. Low hole concentration-related high P-contact resistivity is still an issue, though. A Mg-free Al (Ga) N/h-BN nanowire heterostructure was created in 2017 by Canadian researchers, and at normal temperature, the hole concentration reached 10^{20} cm^{-3}, significantly increasing the epitaxial layer's order of magnitude. And can show high electrical efficiency. In addition, it effectively limits the charge carriers, and EQE first increases with current injection, and then decreases due to saturation [7] [9]. Recently, researchers have also tried other types of electrodes. In 2023, Liao Zhefu and others successfully improved the EQE and WPE of DUV LED by using Ni/Rh/Ni/Au P-type electrode [10].

3.3. Packaging technology

In packaging technology, deep ultraviolet LED is different from white LED. Compared with the organic materials commonly used in white light, because of the short wavelength and high energy of deep ultraviolet light, organic materials will be degraded by ultraviolet light for a long time, affecting the light efficiency and reliability. Regarding packaging technology, semi-inorganic and all-inorganic packaging technologies are more commonly used now. Semi-inorganic packaging involves attaching the deep ultraviolet LED chip to the packaging substrate's cavity and then fixing the Quartz cover with organic adhesive. It reduces the problem of ultraviolet degradation, but the organic bonding materials will still fail with time. For this problem, one is to develop organic transparent materials that are resistant to ultraviolet light. One is not to use organic materials [3].

Fluorine resin is the best organic transparent material that can resist ultraviolet light. In the research of Hirano, meijo university, Japan, through comparative analysis, S-type fluororesin has the highest transmittance. However, it has high cost, insufficient heat resistance and non-airtightness, so its application cannot be popularized. However, all-inorganic packaging technology does not have this problem. Inorganic transparent materials include Shi Ying glass, sapphire, etc. Sapphire is expensive and difficult to process. Quartz has a high transmittance of more than 90% and good mechanical strength and heat resistance, so it is a good choice. The airtight packaging of deep ultraviolet LED is realized by using all inorganic materials, avoiding the use of organic materials, thus improving the reliability of deep ultraviolet LED. With the continuous improvement of the performance of deep ultraviolet LED chips, all-inorganic airtight packaging technology can ensure the long-term working performance of deep ultraviolet LED devices, especially the long-term reliability in harsh environments [3][4][11].

The packaging structure has three-dimensional glass cover plate and three-dimensional ceramic substrate packaging forms. At present, there are many preparation technologies of three-dimensional ceramic substrates, which meet certain requirements [3].

The chip is glued to the ceramic substrate dam for deep ultraviolet LED packaging, the flat glass cover plate is bonded to the ceramic substrate dam, and the interior of the dam is filled with inert gas or air. Light is reflected at the interfaces between the chip and the air and between the glass and the air in this package arrangement because of the influence of the different refractive indices of the materials. This reflection loss will lower the deep ultraviolet LED's light effectiveness. It is necessary to adopt some methods to suppress the reflection loss, including thin film coating and nanostructure for suppressing Fresnel reflection, hemispherical lens for suppressing total reflection, surface roughening, and nano-particle doping packaging layer. Thin film coating uses the destructive interference of single or multi-layer films to suppress reflection, but this method is only suitable for anti-reflection with narrow spectrum and small incident angle, and it is necessary to strictly control the refractive index, thickness and quality of the film. Nanostructures have good anti-reflection, and sub-wavelength nanostructures can form a graded refractive index dielectric layer at the interface, so that the incident light can smoothly enter another medium from one medium, effectively reducing the Fresnel reflection. In order to reduce the Fresnel reflection loss, Yan et al. of Rensselaer Institute of Technology in the United States prepared an omnidirectional anti-reflection film coating on the sapphire substrate of the chip by oblique angle deposition method, which realized the gradual refractive index transition from the sapphire substrate to the air and improved the light extraction efficiency of deep ultraviolet LED by 8% [3] [4].

4. Conclusion

As an ideal semiconductor material, Gallium aluminum nitride stands out in the deep ultraviolet LED field. AlGaN-based deep ultraviolet LED has attracted much attention in disinfection and secret communication because of its adjustable emission wavelength, small size, long life and environmental protection. The highest deep ultraviolet LED manufactured to date, however, has an external quantum efficiency of just 20.3%, and the majority of its WPE is still below 10%. The problem of insufficient light efficiency prevents it from being used in large quantities. These reasons are mainly related to chip-level epitaxy technology, doping technology, and packaging materials and technology. This paper summarizes and evaluates these problems to try to conclude the current development situation and the direction of further exploration in the future.

In the past twenty years, epitaxial and doping technology at the chip level have been studied more and greatly improved. The selection of substrate and buffer layer materials is the primary aspect of epitaxial technology. N-type and P-type doping are the two main types used in doping technology; P-type doping is particularly problematic. In P-type doping, researchers tried Mg, superlattice and other doping. In addition, this paper introduces Ni doping, which has been tried more recently. It can be seen that both EQE and IQE have been improved through the improvement at the chip level. However, P-doping research has stagnated to some extent, and there is no good way to improve electronic efficiency.

Inorganic materials are used in packaging technology. Researchers mainly use thin film coatings and nanostructures to suppress Fresnel reflection and hemispherical lenses to suppress total reflection. This method improves the low light extraction efficiency and light efficiency. Compared with the chip level, the research on the packaging level is less and newer, and there is still much room for improvement.

In view of the more research on the chip level and a certain degree of stagnation, the conclusion of the future research direction in this paper is to pay attention to the packaging level. There are few attempts in selecting packaging materials and packaging structure, and some performance improvements are obvious after making relevant changes. Maybe this is a good breakthrough.

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