## Letters

# Aluminum Nitride Deep-ultraviolet Lightemitting Diodes

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### Abstract

We have successfully fabricated an aluminum nitride light-emitting diode (LED) and observed ultraviolet light with a wavelength of 210 nm. This is the shortest wavelength ever observed from any semiconductor. This LED represents a major step towards replacing large, toxic, and low-efficiency gas light sources with compact, harmless, and high-efficiency semiconductor light sources. The application fields of these LEDs include environmental protection, nanotechnology, and information technology.

#### 1. Introduction

The shortest-wavelength color of light that is visible to the human eye is violet. As shown in **Fig. 1**, light with wavelengths shorter than 400 nm is called ultraviolet (UV) light: that from 300 to 400 nm is called near-UV light, that from 200 to 300 nm is called deep-UV light, and that shorter than 200 nm is called vacuum-UV light. Since vacuum-UV is absorbed by air, deep-UV light is the shortest wave-

length that can be used in our living environment.

The deep-UV light sources available at present are gas light sources, such as mercury lamps or gas lasers. These contain toxic substances, which cause serious environmental problems. Moreover, gas lasers require frequent supplies of gas and are large and inefficient. Therefore, replacing these gas light sources with semiconductor light-emitting devices, such as light-emitting diodes (LEDs) and laser diodes (LDs), would save space and greatly improve relia-



Fig. 1. UV light sources.

† NTT Basic Research Laboratories Atsugi-shi, 243-0198 Japan Email: taniyasu@will.brl.ntt.co.jp bility and efficiency. In addition, semiconductor devices are durable and portable. These features will be advantageous for a variety of new applications.

#### 2. Semiconductor UV light sources

The crystal structures and properties of widebandgap semiconductors are shown in **Fig. 2**. Gallium nitride (GaN) high-brightness blue LEDs and violet LDs are now commercially available [1], [2]. However, as shown in Fig. 1, the shortest wavelength of GaN is 365 nm, which is in the near-UV region. Aluminum nitride (AlN) is a direct-bandgap semiconductor like GaN and has a direct-bandgap energy of 6 eV, the highest among available semiconductors [3], [4]. Therefore, AlN light-emitting devices have been theoretically expected to emit light with a wavelength of 210 nm, which is the shortest value among semiconductors. Diamond and boron nitride (BN) have wide bandgap energies close to that of AlN, but they are indirect-bandgap semiconductors, so their emission efficiencies are much lower than those of direct-bandgap semiconductors. Therefore, diamond and BN are unsuitable for light-emitting devices.

AlN light-emitting devices are expected to have a wide range of applications. The physical properties and device applications of AlN are shown in **Table 1** in comparison with those of GaN. The 210-nm emission wavelength of AlN is 1.8 times shorter than that of GaN, which means that its photon energy is 1.8 times higher. In fact, it is high enough to kill bacteria and viruses and decompose very stable substances, such as dioxin and polychlorinated biphenyls (PCBs), which have caused serious environmental problems all over the world. Therefore, AlN light-emitting devices are expected to be used in environmental protection equipment.

On the other hand, the diameter of a laser spot is inversely proportional to the wavelength. Therefore, the spot size of an AlN LD will be the reciprocal of 1.8 times as large as (= 0.56 times) that of a GaN LD. Once a high-power AlN LD has been developed, it

Device applications



Fig. 2. Crystal structures and properties of wide-bandgap semiconductors.

Dhusiaal proportion				Feature	Ratio	Usage	Application field
Light		AIN Ratio (to GaN)	/	High energy (energy ratio)	1.8 times	Decomposition of dioxins and PCBs; destruction of bacteria and viruses	Environment
emission energy	6.0 eV	1.8 times		Small spot size (wavelength	1.8 times	Nanofabrication on the scale of tens	Nano- technology
Emission wavelength	210 nm	1/1.8 times		High resolution (square of wavelength)	3 times	High-capacity optical storage devices	Information technology

Table 1.	Physical	properties	and device	applications	of AIN

will focus light to spots only tens of nanometers in diameter and will be used for nanometer-scale fabrication. Since the area of a laser spot is inversely proportional to the square of the wavelength, AlN LDs will enable the capacity of optical recoding devices like DVD (digital video disc) players to be increased by three times compared with ones using GaN LDs.

#### 3. Fabrication of high-purity AlN

Semiconductor light-emitting devices generally require n-type and p-type layers obtained by intentional doping of the base material. We clarified that the major problems limiting the doping of AlN are high defect density and high impurity concentration. As shown in Fig. 2, in AlN crystal, the aluminum (Al) and nitrogen (N) atoms should ideally be ordered periodically. However, there is inevitably a thermal equilibrium of point defects, which cause vacancies of Al or N atoms. Furthermore, unintentional impurities, such as oxygen, cause crystal defects. Moreover, if intentionally introduced dopant atoms do not substitute for Al or N atoms regularly, interstitial atoms or vacancies are produced. On the other hand, the lattice mismatch between AlN and the substrate generates another type of crystal defect, called dislocations. Defects and impurities in doped AlN capture generated electrons or holes, preventing the formation of n-type and p-type layers. This was an insurmountable obstacle until now. The challenge was to carefully control the doping and reduce the dislocation density.

Al and N atoms are strongly attracted to each other. During crystal fabrication, secondary reactions between Al and N source gases can therefore occur easily, as shown in **Fig. 3**. Moreover, the fabrication temperature of AlN has usually been as low as 1000°C, which prevents the movement of the atoms on the crystal surface. These characteristics lead to the incorporation of crystal defects and impurities.

These problems have been overcome by developing a high-purity AlN crystal fabrication technique. We constructed an AlN fabrication system that suppresses secondary reactions between Al and N source gases by increasing the gas flow velocity and raising the fabrication temperatures to as high as 1200°C. As a result, we were able to decrease the crystal defect density and impurity concentration by more than one order of magnitude and produce high-purity AlN crystal, which we use to create n-type and p-type AlN.

#### 4. N-type and p-type doping

Having obtained high-purity AlN, the next step was to develop practical n-type and p-type doping techniques for AlN. We obtained n-type AlN by doping silicon (Si) atoms into the high-purity AlN. As shown in **Fig. 4**, when a Si atom with four valence electrons, a negatively charged electron is donated to the AlN. From the temperature dependence of the electron concentration, we estimated that the Si ionization energy was 250 meV. We also studied the elec-



Fig. 3. High-purity AIN crystal fabrication.







Fig. 5. Device structure of AIN deep-UV LED.

tron scattering mechanism and clarified that crystal defects limit the electron mobility. In fact, by decreasing the crystal defects, we increased the room-temperature mobility to 426 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup>, the highest value ever reported for n-type AlN [5]. This attests the high quality of the AlN.

On the other hand, p-type AlN was successfully obtained by doping magnesium (Mg) atoms into the high-purity AlN after thermal annealing in nitrogen (N<sub>2</sub>) ambient. When a Mg atom with two valence electrons substitutes for an Al atom with three valence electrons, a positively charged hole is created in the AlN. However, during fabrication, hydrogen (H) atoms are incorporated into the Mg-doped AlN from sources and they passivate the Mg atoms. As a result, the as-grown Mg-doped AlN is insulating. By applying thermal annealing in N<sub>2</sub>, we caused the H atoms to desorb with the result that the Mg-doped AlN changed from insulating to p-type. From the temperature dependence of the hole concentration, we estimated that the Mg ionization energy was 630 meV. Because this ionization energy is very high, the hole concentration in the p-type AlN is still very low for practical devices at room temperature.

#### 5. Fabrication of AIN deep-UV LEDs

A fabricated AIN LED consisting a high-purity AlN light-emitting layer sandwiched between p-type and n-type AlN layers is shown in **Fig. 5**. In the LED, holes from the p-type AlN and electrons from the ntype AlN are supplied to the light-emitting layer. When holes and electrons combine, light is emitted. The n-type and p-type superlattices in the LED structure were used to reduce the contact resistance of the electrodes.



Fig. 6. 210-nm deep-UV light emission from AIN LED.

The light emission spectrum of the AlN LED is shown in **Fig. 6**. When a forward voltage was applied to the AlN LEDs, we successfully observed deep-UV light attributed to the near-band-edge emission in AlN at a wavelength of approximately 210 nm. This emission wavelength is the shortest ever observed from any semiconductor [6]. The output power of the near-band-edge emission at  $\lambda = 210$  nm was measured to be about 0.02 µW at a DC current of 40 mA. The external quantum efficiency was estimated to be on the order of  $10^{-6}\%$ , which is much lower than that for commercial visible LEDs ( $\eta_{ext} = 1-10\%$ ). In our AlN LED, the low external quantum efficiency resulted from the low hole concentration in the p-type AlN layer.

#### 6. Conclusion

We have successfully demonstrated a deep-UV AlN LED with a wavelength of 210 nm. This is the shortest wavelength ever observed from any semiconductor. Although this is a major breakthrough, practical devices will require much higher output power and quantum efficiency as well as a longer operating lifetime and lower operating voltage. As the next step, we plan to turn our attention to improving the output power.

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