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P-Type Conduction in Mg-Doped GaN Treated with Low-Energy Electron Beam Irradiation (LEEBI)

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Distinct p-type conduction is realized with Mg-doped GaN by the low-energy electron-beam irradiation (LEEBI) treatment, and the properties of the GaN p-n junction LED are reported for the first time. It was found that the LEEBI treatment drastically lowers the resistivity and remarkably enhances the PL efficiency of MOVPE-grown Mg-doped GaN. The Hall effect measurement of this Mg-doped GaN treated with LEEBI at room temperature showed that the hole concentration is $\sim 2\cdot 10^{16}$ cm^{-3}, the hole mobility is ~ 8 cm^2/V·s and the resistivity is $\sim 35\ \Omega\cdot$cm. The p-n junction LED using Mg-doped GaN treated with LEEBI as the p-type material showed strong near-band-edge emission due to the hole injection from the p-layer to the n-layer at room temperature.

KEYWORDS: GaN, GaN:Mg, LEEBI treatment, Hall effect, p-type conduction, p-n junction LED, UV-LED

Gallium nitride (GaN) is one of the most promising materials for application to blue, violet and ultraviolet (UV) light emitting devices such as light emitting diodes (LEDs) and laser diodes (LDs), because it has a direct transition type band structure and its band gap is 3.39 eV at room temperature (RT).

For the preparation of single-crystalline GaN, heteroepitaxial growth on a sapphire substrate is used. Because of the large lattice mismatch and the large difference in the thermal expansion coefficient between GaN and sapphire, it used to be fairly difficult to grow high-quality epitaxial GaN film with a flat surface free from cracks. These problems have been overcome by the prior deposition of a thin AlN as a buffer layer before the growth of GaN by metal-organic vapor phase epitaxy (MOVPE).[1,2] The film uniformity, crystalline quality, luminescence and electrical properties of the GaN films were improved remarkably, and efficient metal/Zn-doped highly resistive i-GaN/undoped n-GaN (m-i-n)-structured blue LEDs were developed[3,4] by using this AlN buffer layer technique.

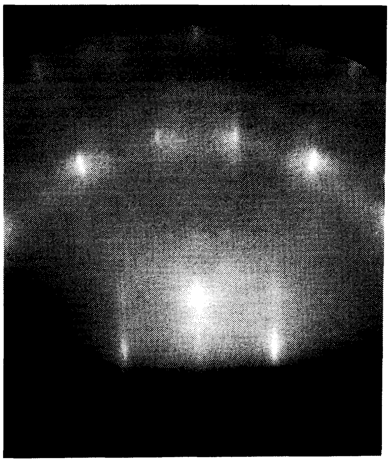
However, in order to improve further the performance of the blue LED and to realize a LD, it will be necessary to achieve conductivity control of the GaN film and, in particular, development of a p-type GaN film. Although Madar *et al.*[5] reported on a p-type material, their crystals, prepared by high-pressure solution growth, were polycrystalline, and their properties have not been described in detail. Up to now, there have been no reports concerning the GaN p-n junction LED.

Recently, we found out that the luminescence properties of Zn-doped[6] or Mg-doped GaN (GaN:Mg) had been changed remarkably by treatment with low-energy electron beam irradiation (LEEBI), the accelerating voltage of which was far below the subthreshold energy for atom displacement. Not only the luminescence properties, but also the electrical properties are found to be changed greatly, especially in the case of the LEEBI treatment of the GaN:Mg film. The as-grown GaN:Mg is highly resistive. Upon LEEBI treatment, the resistivity decreases drastically and the GaN:Mg film tends to show p-type conduction.

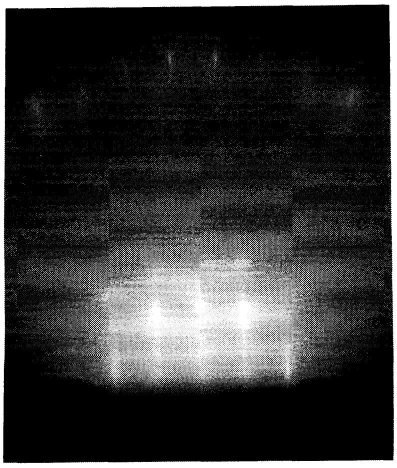
This is the first report on both the single crystalline GaN film showing the distinct p-type conduction and the characteristics of the p-n junction GaN LED.

A horizontal type MOVPE reactor operated at atmospheric pressure was used for the growth of GaN film. As a substrate, (0001) sapphire was used. Trimethylgallium (TMG), trimethylaluminum (TMA) and ammonia (NH_3) were used as the Ga, Al and N sources, respectively. Bis-cyclopentadienyl magnesium (Cp_2Mg) was used as the Mg source. At first, the substrate was heated at 1150°C in a stream of hydrogen to clean the surface. Then the substrate temperature was lowered to 600°C, and an AlN layer 50 nm thick was deposited as a buffer layer.[1,2] During the deposition, the flow rates of TMA and NH_3 were kept at 3.6 μmol/min and 1.5 SLM, respectively. After deposition of the AlN buffer layer, the substrate temperature was raised to 1040°C to grow GaN:Mg film $2\sim 3$ μm thick. The Mg concentration in the GaN:Mg film was a few 10^{20} cm^{-3}. The GaN:Mg film was then treated with LEEBI.[6] The accelerating voltage of the incident electrons was kept at 10 kV, and the electron beam spot size was 60 μmϕ. The emission current of the electron beam was 60 μA. During LEEBI treatment, the sample was kept at room temperature. The conditions of LEEBI treatment are discussed in detail elsewhere,[7] but the mechanism of the LEEBI treatment has not been completely clarified.

The crystalline quality of the GaN:Mg film was confirmed by the reflection high-energy electron diffraction (RHEED) pattern and the double-crystal X-ray rocking curve (DCRC) measurement. Figure 1 shows an example of the RHEED patterns of the GaN:Mg film for the azimuths $[11\bar{2}0]$ (Fig. 1(a)) and $[10\bar{1}0]$ (Fig. 1(b)). Kikuchi lines are clearly observed, indicating that the GaN:Mg film is a single crystal having high crystalline quality. The full width at half-maximum of the DCRC from the $(20\bar{2}4)$ plane of the GaN:Mg film was about 4 min, which is comparable or slightly broader than that of



(a)



(b)

Fig. 1. RHEED patterns of the GaN:Mg film on (0001) sapphire substrate for the azimuths [11$\bar{2}$0] (Fig. 1(a)) and [10$\bar{1}$0] (Fig. 1(b)). Mg concentration in the GaN:Mg film is 1.0×10^{20} cm^{-3}.

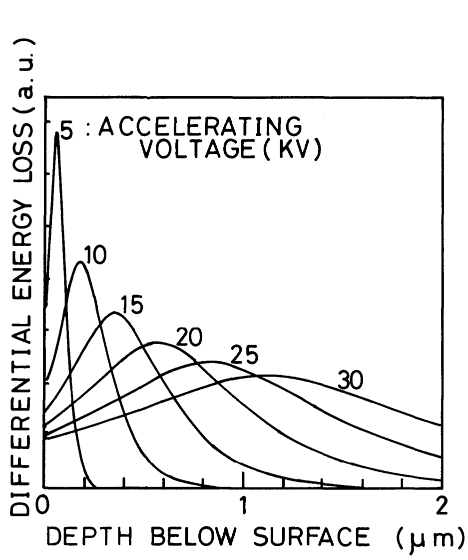


Fig. 2. Estimated change of the energy loss of the incident electrons in GaN as a function of the accelerating voltage of the incident electrons.

the undoped GaN film grown using the AlN buffer layer. The RHEED pattern and the profile of DCRC of the GaN:Mg film were not changed by the LEEBI treatment.

Aluminum electrodes for ohmic contacts were deposited to examine the electrical properties of the GaN:Mg film. The current-voltage (*I-V*) characteristics of the as-grown and the LEEBI-treated GaN:Mg film clearly show that the LEEBI treatment lowers the resistivity of the GaN:Mg film by more than five orders of magnitude. The Hall effect measurement was performed at RT in a Van der Pauw configuration. The as-grown GaN:Mg film is highly resistive, which makes it difficult to measure the Hall effect. The GaN:Mg film treated with LEEBI clearly shows the p-type conduction with resistivity of $\sim 35\ \Omega\cdot$cm. Considering the energy of the incident electrons, the penetration depth of the incident electrons is estimated to be around 500 nm. Figure 2 shows the estimated change of the energy loss of the incident electrons in GaN as a function of the accelerating voltage of the incident electrons.[8] The hole concentration is estimated to be $\sim 2\times10^{16}$ cm^{-3} and the mobility to be ~ 8 cm^2/V$\cdot$s. Results of the Hall effect measurements are summarized in Table I.

On the basis of the results, p-n junction LEDs were fabricated. Undoped n-type GaN (*n*: 2×10^{17} cm^{-3}) film 3 μm thick was grown on the sapphire substrate using the AlN buffer layer, followed by GaN:Mg film 500 nm thick with a Mg concentration of 2×10^{20} cm^{-3}. Then a 2 mm $\times$ 2 mm portion was treated with LEEBI, and an Al electrode of 500 μmϕ was deposited on it. The Al electrode was also deposited on the side of the n-type GaN for ohmic contact. Figure 3 shows the structure of the p-n junction LED. Because of the high resistivity of the as-grown GaN:Mg film, the leakage current between the upper part and the side part of the electrode is negligibly small. A typical example of the *I-V* characteristics, and the DC electroluminescence (EL) spectrum measured at RT of the p-n junction LED are shown in Figs. 4(a) and 5(a), respectively. Those of the conventional m-i-n LED, which uses the as-grown GaN:Mg film, are also shown in

Table I. The electrical properties of the as-grown and the LEEBI treated GaN:Mg with Mg concentration of 2×10^{20} cm^{-3}. We assume the thickness of the LEEBI treated GaN:Mg film to be 500 nm.

LEEBI treated	$\rho\sim35\ \Omega\cdot$cm,	$p\sim2\times10^{16}$ cm^{-3},	$\mu\sim8$ cm^2/V$\cdot$s
As grown	highly resistive, $\rho>10^8\ \Omega\cdot$cm		

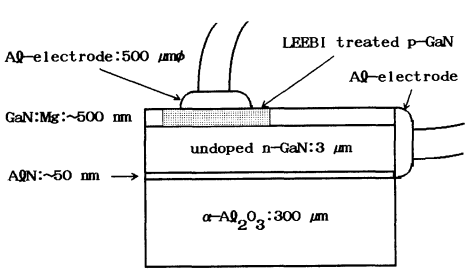


Fig. 3. The structure of the p-n junction LED.

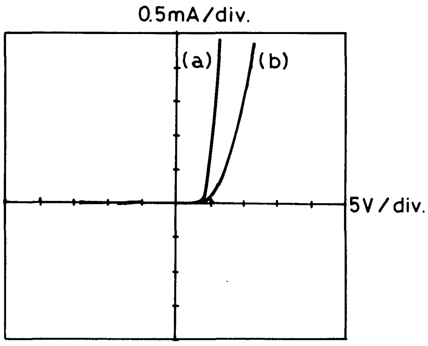


Fig. 4. *I-V* characteristics of the p-n junction LED (Fig. 4(a)) and the conventional m-i-n LED (Fig. 4(b)).

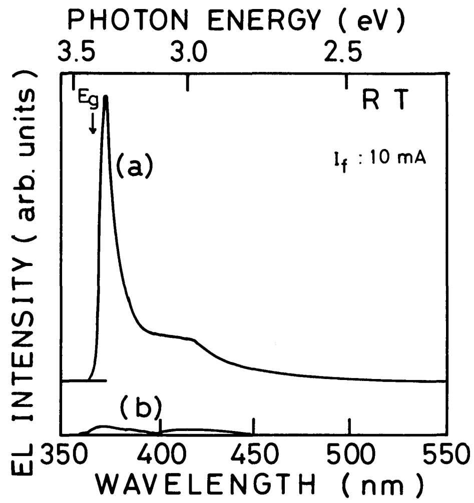


Fig. 5. DC-EL spectrum of the p-n junction LED (Fig. 5(a)) and the conventional m-i-n LED (Fig. 5(b)), measured at room temperature.

Figs. 4(b) and 5(b) for comparison. The EL spectrum of the p-n junction LED clearly shows the strong near-band-edge UV emission. To clarify in which part of the p-n junction LED the near-band-edge UV-EL was emitted, cathodoluminescence (CL) was measured by changing the accelerating voltage of the exciting electrons. When accelerating voltage was lower than 10 kV, only violet CL was detected. As the accelerating voltage increased, the near-band-edge UV emission came to dominate the CL spectrum of the p-n junction LED. Therefore, it is thought that the near-band-edge UV-EL is emitted in the undoped n-type GaN film. This shows that holes are injected efficiently from the p-type GaN:Mg film to the undoped n-type film.

In summary, a distinct p-type GaN film has been realized for the first time, using a GaN:Mg film grown by MOVPE followed by LEEBI treatment. A GaN UV-LED with a p-n junction was also developed by means of this new process.

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