Compensation effect of Mg-doped \(a\)- and \(c\)-plane GaN films grown by metalorganic vapor phase epitaxy

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The electrical and optical properties of Mg-doped \(a\)- and \(c\)-plane GaN films grown by metalorganic vapor phase epitaxy were systematically investigated. The photoluminescence spectra of Mg-doped \(a\)- and \(c\)-plane GaN films exhibit strong emissions related to deep donors when Mg doping concentrations are above \(1 \times 10^{20}\) cm\(^{-3}\) and \(5 \times 10^{19}\) cm\(^{-3}\), respectively. The electrical properties also indicate the existence of compensating donors because the hole concentration decreases at such high Mg doping concentrations. In addition, we estimated the \(N_d/N_A\) compensation ratio of \(a\)- and \(c\)-plane GaN by variable-temperature Hall effect measurement. The obtained results indicate that the compensation effect of the Mg-doped \(a\)-plane GaN films is lower than that of the Mg-doped \(c\)-plane GaN films.

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1. Introduction

Commercially available nitride-based light-emitting devices are grown along the polar \(c\)-direction \([1–3]\). Therefore, the external quantum efficiency is limited owing to charge separation in the quantum wells caused by spontaneous and piezoelectric polarization \([4,5]\). A large piezoelectric field is one of the most critical factors causing the decreased efficiency in the green region. It is possible to inhibit such polarization effects by growing device structures on a nonpolar plane, such as an \(a\)-plane or \(m\)-plane \([6]\). Therefore, the investigation of p-type group III nitride-based semiconductors is an important research field, because p-type layers with high hole concentrations are highly advantageous for improving device performance characteristics. However, the hole concentration of Mg-doped GaN at room temperature (RT) is limited to a few percent of the Mg concentration. In previous studies, the Mg acceptor activation energies of \(c\)-plane GaN with varying Mg concentration were found to range from 190 to 112 meV, and the Mg acceptor activation energy of \(a\)-plane GaN with a Mg concentration of \(4.0 \times 10^{19}\) cm\(^{-3}\) was found to be 118 meV \([7–9]\). In this study, we examined the optical and electrical properties of Mg-doped GaN at various Mg concentrations. We also investigated the activation energies of the Mg acceptors in \(a\)- and \(c\)-plane GaN with Mg concentrations from \(5.4 \times 10^{18}\) to \(2.0 \times 10^{20}\) cm\(^{-3}\). The increase in the Mg doping level led to compensation effects in p-type \(a\)- and \(c\)-plane GaN identified by a lower hole concentration and the deep-level PL emission.

2. Experiments

The samples were grown by metalorganic vapor phase epitaxy (MOVPE). Trimethylaluminum (TMA), trimethylgallium (TMG), ammonia (NH\(_3\)), and ethyl-bis-cyclopentadienyl magnesium (Et-Cp\(_2\)Mg) were used as the source gases. Mg-doped \(a\)-plane GaN films were fabricated on sidewall-epitaxial-lateral-overgrown (SELO) GaN grown on \(r\)-plane sapphire substrates by MOVPE \([10,11]\). Fig. 1(a) schematically shows the structure of the Mg-doped \(a\)-plane GaN sample. A 150-nm-thick \(a\)-plane AlN layer and a 500-nm-thick \(a\)-plane AlGaN layer were grown at approximately 1030 °C on an \(r\)-plane sapphire substrate. Then, an unintentionally doped GaN film of about \(1.2\) \(\mu\)m thickness was grown \([12]\). After growing GaN, the wafer was removed from the reactor. A Ni/SiO\(_2\) film was deposited and patterned by photolithography and conventional reactive ion etching to produce periodic grooves along the \(\langle 1 \bar{1} 0 0 \rangle\)-axis with a width of \(3 \mu\m\). It was necessary to etch the grooves down to the sapphire substrate to promote GaN growth from the sidewalls. Furthermore, the sample was reloaded into the reactor to grow a 12-\(\mu\m\)-thick GaN layer. We thus obtained high-crystalline-quality \(a\)-plane GaN by SELO \([13]\). The average concentrations of basal stacking faults and threading dislocations over the entire area were \(~4 \times 10^4\) cm\(^{-1}\) and \(~2 \times 10^8\) cm\(^{-2}\), respectively. Then,
0.5-μm-thick Mg-doped GaN films were grown. If Mg-doped α-plane GaN films were grown on high-defect-density GaN, these defects might have caused a decrease in hole mobility and an increase in resistivity [14]. Therefore, the SELO technique is necessary for the realization of higher-performance p-type α-plane GaN. For comparison, we also prepared Mg-doped c-plane GaN grown on c-plane sapphire substrates, as shown in Fig. 1(b). These samples were grown on 2-μm-thick GaN deposited on c-plane sapphire covered with a low-temperature buffer layer. Mg-doped α- and c-plane GaN films were successively grown at different Et-Cp₂Mg source gas flow rates. Secondary ion-microprobe mass spectrometry (SIMS) measurements were conducted to measure the Mg concentration. After the growth, all the Mg-doped samples were annealed at 700 °C for 5 min in nitrogen ambient to activate the Mg acceptors. We used Ni/Au as ohmic electrodes. We carried out van der Pauw Hall effect measurement to determine the carrier concentration of Mg-doped GaN at RT. All α-plane samples have an isotropic property. To estimate the activation energy of the Mg acceptors, variable-temperature Hall effect measurement was also performed in the temperature range from 180 to 300 K.

3. Results

AFM measurements were carried out in a 5 μm × 5 μm area to observe the surface morphologies of (a) undoped α- and c-plane GaN, (b) Mg-doped α- and c-plane GaN with a Mg concentration of 1–2 × 10¹⁹ cm⁻³, and (c) Mg-doped α- and c-plane GaN with a Mg concentration of 1–2 × 10²⁰ cm⁻³, as shown in Fig. 2. At the highest doping level, the surface of the c-plane samples became rough due to the formation of hexagonal hillocks, as observed previously. The surface roughness of Mg-doped c-plane GaN was caused by the formation of inversion domain boundaries [15,16]. In contrast, Mg-doped α-plane GaN exhibited a much better surface morphology, which was unaffected by the Mg doping.

The PL spectra at RT of Mg-doped α- and c-plane GaN with different Mg concentrations are shown in Fig. 3. The PL spectra of Mg-doped c-plane GaN grown with a Mg concentration of approximately 4 × 10¹⁹ cm⁻³ were dominated by the near-band-edge emission peaking at 3.43 eV and Mg-related emission peaking at 3.29 eV, as shown in Fig. 3(a). The increase in Mg concentration led to deep-level emission at approximately 2.99 eV in the PL spectra. This emission was previously reported for highly Mg-doped GaN. (b) Mg-doped α- and c-plane GaN with a Mg concentration of 1–2 × 10¹⁹ cm⁻³, and (c) Mg-doped α- and c-plane GaN with a Mg concentration of 1–2 × 10²⁰ cm⁻³, as shown in Fig. 2. At the highest doping level, the surface of the c-plane samples became rough due to the formation of hexagonal hillocks, as observed previously. The surface roughness of Mg-doped c-plane GaN was caused by the formation of inversion domain boundaries [15,16]. In contrast, Mg-doped α-plane GaN exhibited a much better surface morphology, which was unaffected by the Mg doping.

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Mg-doped GaN and attributed to MgGa–VN complexes showing deep-donor–acceptor-pair characteristics [17]. Increase in the Mg concentration leads to compensation effects with Mg Ga–VN complexes identified by low hole concentrations [18,19]. This also suggests that it is difficult to achieve a high hole concentration in c-plane GaN with a high doping level. On the other hand, deep-level emission in Mg-doped α-plane GaN was only observed at Mg concentrations exceeding \(1 \times 10^{20}\) cm\(^{-3}\) as shown in Fig. 3(b), indicating that highly Mg-doped α-plane GaN with a high hole concentration can be realized.

Fig. 4 shows the hole concentrations of α- and c-plane Mg-doped GaN at RT as a function of Mg concentration. The hole concentration of Mg-doped c-plane GaN increased with increase in Mg concentration up to \(\sim 4 \times 10^{19}\) cm\(^{-3}\). When the Mg concentration exceeded \(\sim 4 \times 10^{19}\) cm\(^{-3}\), the hole concentration decreased sharply. In contrast, in Mg-doped α-plane GaN, the hole concentration increased with increase in Mg concentration up to \(\sim 4 \times 10^{19}\) cm\(^{-3}\). When the Mg concentration exceeded \(\sim 4 \times 10^{19}\) cm\(^{-3}\), the hole concentration decreased slightly. Mg-doped α-plane GaN with RT hole concentration as high as \(1.8 \times 10^{19}\) cm\(^{-3}\) was achieved. This result shows the feasibility of achieving high-conductivity p-type α-plane GaN.

Fig. 4 shows the hole concentrations of Mg-doped α- and c-plane GaN after annealing at 700 °C for different Mg concentrations.

Fig. 3. PL spectra of Mg-doped α- and c-plane GaN after annealing at 700 °C for different Mg concentrations.

The correlation between the results obtained from the Hall effect and PL measurements suggests that a hole concentration of order of \(10^{18}\) cm\(^{-3}\) with a reduced compensation effect can be achieved in Mg-doped α-plane GaN with a Mg concentration exceeding \(2\)–\(4 \times 10^{19}\) cm\(^{-3}\). Owing to improvements in material, it is expected that the compensating donor concentration will be reduced. The free-hole concentration \(p\) of a partially compensated p-type semiconductor with acceptor concentration \((N_A)\), donor concentration \((N_D)\), and acceptor activation energy \((E_A)\) is given by Eq. (1), where \(T\) is the temperature, \(k\) is the Boltzmann constant, \(g\) is the acceptor degeneracy (assumed to be 2), \(N_i\) is the effective density of states at the valence band edge, as shown in Eq. (2), and \(m^*_h\) is the average hole effective mass of GaN [20]:

\[
p(p+N_D) = \frac{N_V}{g} \exp \left( - \frac{E_A}{k_BT} \right)
\]

\[
N_V = 2 \left( \frac{2\pi m^*_h k_BT}{\hbar^2} \right)^{3/2}
\]

The temperature dependence of the hole concentrations of α- and c-plane Mg-doped GaN with different Mg concentrations is shown in Fig. 5. The solid lines in Fig. 5 indicate the results calculated using Eq. (1). Table 1 shows the fitting parameters obtained by the Hall effect measurement of Mg-doped α- and c-plane GaN. The Mg acceptor activation energies of the α- and c-plane GaN were the same at various Mg concentrations. The lowest activation energies of the Mg acceptors of α- and c-plane GaN were both 123 meV, at which the hole concentrations were \(1.2 \times 10^{18}\) and \(1.0 \times 10^{18}\) cm\(^{-3}\), the hole mobilities were 7.1 and 4.1 cm\(^2\)/V s, and the resistivities were 0.76 and 1.49 Ω cm.

Fig. 6 shows the \(N_D/N_A\) compensation ratio and Mg acceptor activation energies of α- and c-plane GaN plotted as a function of \(N_A\) concentration calculated from Eq. (1). The Mg acceptor activation energies of α- and c-plane GaN decreased with increase in \(N_A\) concentration. However, when the Mg doping
level exceeded $\sim 2-3 \times 10^{19}$ cm$^{-3}$, the Mg acceptor activation energy started to increase. We also observed that the calculated compensating donor concentration increased markedly as the Mg doping level increased. The activation energy of Mg is known to reduce with increase in the acceptor concentration\[8\]. Exceeding the Mg doping concentration of $\sim 2-3 \times 10^{19}$ cm$^{-3}$, donor-like native defects caused by MgGa–VN complexes are created\[18,19\]. These defects compensate the acceptor concentration, and may result in the increase of the activation energy. Thus, the ND/NA compensation ratio also increased with increase in Mg doping level. These results clearly show that the compensation effects of Mg-doped $a$-plane GaN were less pronounced than those of Mg-doped $c$-plane GaN.

### 4. Conclusion

We have examined the optical and electrical properties of Mg-doped $a$- and $c$-plane GaN as a function of Mg doping level. PL measurements indicated that Mg-doped $a$-plane GaN has a low density of deep donors. In Mg-doped $a$-plane GaN, a hole concentration as high as $1.8 \times 10^{18}$ cm$^{-3}$ was achieved. The concentration of compensating donors in Mg-doped $a$-plane GaN was lower than that in Mg-doped $c$-plane GaN at various Mg concentrations. Thus, the feasibility of achieving high-hole-concentration Mg-doped $a$-plane GaN layers was demonstrated.

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### References