Photoluminescence and photocurrent studies of p-type GaN with various thermal treatments

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Received 3 May 2001; accepted 9 October 2001
Communicated by C.R. Abernathy

Abstract

We present a photoluminescence and photocurrent study of the Mg-doped p-type GaN grown on sapphire substrate by metalorganic chemical vapor deposition. In photoluminescence spectra, either a strong blue emission at 2.88 eV or weak band-edge-related photoluminescence peaks were observed at room temperature, depending on the initial condition of annealing. The photocurrent spectra exhibit a main band located at 3.01 eV, and an additional band around 1.22 eV depending also on the annealing condition. The photoluminescence and photocurrent results suggest that the photocurrent peak at 1.22 eV is associated with the absorption from the valence band edge to the deep donor state located above the Mg acceptor level.

PACS: 78.55.Cr; 73.50.Pz; 71.55.Eq


1. Introduction

Gallium nitride (GaN) has been one of the most promising materials for blue-ultraviolet (UV) lasers, short wavelength radiation detectors and high-temperature electronic devices. This is evident from several impressive achievements in the last few years, including the light-emitting diodes (LED) [1], laser diodes (LD) [2], solar-blind UV detectors [3], and high-temperature transistors [4]. The application of GaN for optoelectronic devices requires a detailed knowledge of its fundamental optical properties. In this respect, the so-called yellow luminescence, a deep level defect-induced transition which affects the efficiency of optoelectronic devices has been a problem that attracts attention of many researchers [5–7]. The yellow luminescence, a broad band centered around 2.2 eV, is observed in both undoped and doped n-type GaN samples, regardless of the growth methods, such as metalorganic chemical vapor
deposition (MOCVD), molecular-beam epitaxy (MBE), and other growth technique. For Mg-doped GaN, the photoluminescence (PL) property is more complex and depends strongly on the Mg concentration and thermal annealing conditions. The blue emission is the most dominant PL peak in the Mg-doped GaN [8,9], but the yellow emission is also detected upon the excitation below the transition energy of the Mg-related band, 2.9–3.0 eV [10]. This result evidences the existence of the yellow band related defects in both n-type or semi-insulating Mg-doped samples. The photocurrent (PC) spectra can provide insight about the optical properties, especially about defect states in the forbidden gap. Nevertheless, very few works have been reported on the PC study of GaN [11–13], particularly of p-type GaN. In this work, we measured PL and PC spectra of p-GaN epilayers annealed with various conditions.

2. Experiment

The GaN samples investigated in this work were grown in a MOCVD system on (0 0 0 1) oriented sapphire substrate at low pressure. The ammonia and trimethylgallium (TMG) were served as precursors, and the bis-cyclopentadienyl magnesium (Cp₂Mg) was used for the Mg doping. Prior to the growth of the epitaxial layer, a GaN buffer layer with nominal thickness of 25 nm was grown at 500°C. The flow rate of TMG was 150 μmol/min and the flow rate ratio of ammonia to TMG was 2500. The 2 μm-thick epitaxial GaN layers were grown at 1010°C at the growth rate of 2 μm/h. To activate the Mg acceptors, GaN samples were annealed in a rapid thermal annealing (RTA) or a furnace system under N₂ atmosphere. The temperature was raised by 30°C/s and 20°C/min for RTA and a furnace system, respectively. To investigate the effect of annealing process on the optical properties, five types of samples were prepared from two different GaN as-grown epilayers; the annealing time and temperature, and the hole concentration and mobility determined from room temperature Hall-effect measurements are summarized in Table 1. These results manifest that electrical properties are not significantly changed by the annealing conditions employed in this work. The PC spectra of p-type GaN were measured at room temperature since the conductivity of p-type GaN decreases due to the impurity band conduction at low temperature [14,15]. The PC measurements were carried out in a coplanar geometry with two Ni/Au contacts soldered to the GaN surface. The ohmic contact

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Annealing time (min)</th>
<th>Annealing temperature (°C)</th>
<th>Hole concentration (cm⁻³)</th>
<th>Hole mobility (cm²/V s)</th>
<th>Annealing method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample A</td>
<td>5</td>
<td>450</td>
<td>2.08 × 10¹⁷</td>
<td>11.2</td>
<td>RTA (two step)</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>900</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample B</td>
<td>5</td>
<td>500</td>
<td>2.2 × 10¹⁷</td>
<td>13.3</td>
<td>RTA (two step)</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>900</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample C</td>
<td>5</td>
<td>700</td>
<td>2.3 × 10¹⁷</td>
<td>14.2</td>
<td>RTA (two step)</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>900</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sample D</td>
<td>5</td>
<td>900</td>
<td>2.5 × 10¹⁷</td>
<td>12.3</td>
<td>RTA (one step)</td>
</tr>
<tr>
<td>Sample E</td>
<td>50</td>
<td>900</td>
<td>2.4 × 10¹⁷</td>
<td>13.8</td>
<td>Furnace (one step)</td>
</tr>
</tbody>
</table>

*Samples B and D are from one wafer, and the others are from another.
have been confirmed by $I-V$ characteristics. The light beam from a tungsten–halogen lamp passed through a chopper and was dispersed by a monochromator before being illuminated on the sample. The PC signal was picked up with a lock-in amplifier and then recorded by a computer. A bias voltage was supplied by a current source, and the monochromatic photon flux onto the sample was of the order of $10^9$ photons/s. The normalization effect of the incident photon density did not significantly alter the PC spectrum. PL was also excited at room temperature with the 325 nm line of a He–Cd laser.

3. Results and discussion

Room-temperature PL spectra of annealed p-type GaN samples are presented in Figs. 1 and 2. The PL spectra of as-grown epilayers used in this work show only a broad blue band in the range of 2.5–3.0 eV. Fig. 1 shows that samples A, B and C exhibit a strong blue emission band peaked at 2.88 eV with a full-width at half-maximum (FWHM) in the range between 210 and 280 meV. In general, in a heavily Mg-doped GaN, a broad PL band around 2.6–2.9 eV dominates the PL spectrum and is attributed to an optical transition from the conduction band to a deep acceptor [16–18] or to a Mg complex level [19,20] about 0.5–0.55 eV above the valence band or donor–acceptor pair transitions from a deep donor to a shallow Mg acceptor [21,22]. On the other hand, the PL emission of samples D and E at room temperature are completely different from those of samples A, B and C as shown in Fig. 2. Instead of the strong blue emission, four weak PL peaks, P1, P2, P3, and P4, appear in the spectral range between 3.1 and 3.4 eV. There is only a weak PL tail in the blue emission band region, which is similar to the result reported by W. Götz et al. [15]. It is believed that the PL peak, P1, located at 3.39 eV corresponds to the free exciton transition and P3 at 3.26 eV is due to the shallow donor–acceptor transition; P2 and P4 are phonon replicas of P1 and P3, respectively. PL results show that the luminescence property of the p-type GaN strongly depends on the thermal annealing condition, especially the initial stage of
the thermal annealing, even though the exact nature of which is still to be determined.

The PC spectra of the p-GaN measured at room temperature are presented in Figs. 3 and 4. Fig. 3 shows that PC spectra of samples A, B and C exhibit only one broad band, C1, around 3.01 eV with relatively weak intensity. On the other hand, the PC spectra of samples D and E consist of two bands. The main band C1 centered at 3.01 eV has a FWHM of about 400 meV, similar to the values of samples A, B, and C, but is more intense. The second broad band appeared at near infrared region. The main peak of the second band (C2) is located at 1.22 eV, and one shoulder is observed at 1.52 eV (C3). It is interesting to compare PC with PL spectra. Although the PL spectra were quite different for a sample group of A, B, and C from those of D and E, the spectral features in the PC spectra of all the samples are quite similar in the blue absorption region.

The correlation between the main PC band and the strong blue PL appeared in samples A, B, and C suggests that the transition from the conduction band to the acceptor level of the Mg complex induces PL, while the transition from the deep Mg complex level to the conduction band is responsible for PC. On the other hand, we attribute the C2 band peaked at around 1.22 eV in the PC spectra to the absorption from the valence band-edge to a deep donor state similar to the state related to the origin of the yellow band emission in undoped or doped n-type GaN. The yellow band absorption from deep donor state located 2.13 eV below the conduction band edge to the conduction band has been observed in undoped GaN [23,24]. As mentioned earlier, the yellow band emission is generally observed in undoped, n-type doped, and Mg-doped semi-insulating GaN, but not in p-type GaN. Sanchez et al. [10] reported that in Mg-doped GaN, the yellow luminescence is only observed for excitation energies lower than the transition energy of the Mg-related band around 2.9–3.0 eV. Three mechanisms of the yellow band emission have been proposed in the literature. The first is a transition from a shallow donor state to a deep localized acceptor state [5], while the second mechanism describes a transition from a deep double donor to a shallow acceptor state [25].

![Fig. 3. Photocurrent spectra of samples A, B and C at 297 K. Only C1 peak at 3.01 eV is observed with FWHM about 400 meV.](image1)

![Fig. 4. Photocurrent spectra of samples D and E at 297 K. C2 peak at 1.22 eV and a shoulder at 1.52 eV are observed in addition to C1 peak.](image2)
newly proposed mechanism involves a transition from a shallow donor to a deep double donor state [23,26]. Deep level states responsible for the yellow band emission in any of three models mentioned above can give a PC peak at around 1.22 eV. However, as in samples D and E, when the deep level at 1.22 eV is formed, the intensity of the main PC peak C1 at 3.01 eV is enhanced while the blue emission around 2.88 eV in the PL spectrum is quenched; this strongly suggests that the low energy PC band, C2, is associated with the absorption due to the transition from the valence band edge to the deep donor state located above the Mg acceptor level, and this deep donor state is similar to those observed in undoped or n-type GaN in conjunction with yellow luminescence.

In a Mg-doped MOCVD grown GaN, it has been shown theoretically that the H concentration essentially equals the Mg concentration and the H donors and Mg acceptors form electrically neutral complexes [27]. The post-growth annealing dissociates the Mg-H complex and then either removes or neutralizes the H atom in the GaN layer. Our experiment suggests that a deep donor level can be formed above the Mg acceptor level depending upon the initial temperature of annealing. In the case of samples A, B, and C, the photogenerated holes in the PL experiment are trapped at the Mg acceptor level where the radiative recombination takes place. Similarly, the absorption in the PC experiment mainly occurs from the Mg acceptor level to the conduction band. On the other hand, in samples D and E, it seems that electrons from deep donors are captured at the Mg complex level where they recombine with photogenerated holes. Consequently, the blue luminescence is quenched and only the weak band-edge luminescence peaks are observed in the PL experiment. The PC peak at 3.01 eV becomes stronger owing to increased number of electrons in Mg acceptor level. We believe that the PC spectra shown in Fig. 4 are direct spectroscopic evidence showing that there is a deep donor state which have the same origin as those related with the yellow band emission in undoped or n-type GaN. The absence of the yellow luminescence in typical PL spectra excited with above bandgap energies in p-type GaN may be due to a higher efficiency of the Mg-related recombination path. Our results also show that only samples D and E have such a deep donor state, suggesting that the formation of the deep donor state in p-type GaN depends on the thermal annealing condition.

4. Conclusions

The PL and PC spectroscopies have been employed to investigate optical properties of Mg-doped p-type GaN grown by MOCVD. In the PL spectra, either a strong blue emission peak or weak band-edge-related PL peaks are observed at room temperature, showing that the PL property strongly depends on the thermal annealing process. The PC spectra consist of a main band with its dominant peak located at 3.01 eV associated with the Mg acceptor level. Depending upon the annealing condition, the low-energy band located around 1.22 eV appears additionally and is believed to be a direct spectroscopic evidence showing that there exists a deep donor level which can be related with a yellow band emission in GaN. The origin of the deep donor state formed by certain annealing process should be studied further.

Acknowledgements

This work was supported by Grant No. (2000-0-114-002-3) from the basic research program of the Korea Science and Engineering Foundation (KOSEF).

References

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