Mg Doping of 3D Semipolar InGaN/GaN-Based Light Emitting Diodes

Junjun Wang

The effects of different Mg doping concentrations in the main p-GaN layer and the p-GaN capping layer on the electroluminescence (EL) property of three-dimensional (3D) stripe semipolar InGaN/GaN based light emitting diodes (LEDs) were investigated. Secondary ion mass spectrometry (SIMS) analysis revealed the Mq concentration of the 3D semipolar p-GaN, indicating a higher Mg incorporation efficiency on the $\{1011\}$ facet compared to the $\{11\overline{2}2\}$ facet. Low-temperature μ -photoluminescence was measured on a series of 3D LED structures varying the Mq doping concentration. For the LEDs with the $\{10\overline{1}1\}\$ facet, pronounced donor-acceptor-pair (DAP) luminescence at 3.24 eV with characteristic LO-replicas was observed with the molar flow ratio between Cp_2Mq and TMGa $(Cp_2Mq/TMGa)$ of 0.04% and 0.06%. With further increasing $Cp_2Mq/TMGa$ of 0.10% and 0.21%, the DAP band shifts to a broad band emission at a lower energy presenting the emergence of self-compensation. In contrary, self-compensation was not observed up to $Cp_2Mq/TMGa$ of 0.21% for the LEDs with the $\{11\overline{2}2\}$ facet. Thus, the Mg incorporation efficiency on the $\{10\overline{1}1\}$ facet is concluded to be higher than that on the $\{11\overline{2}2\}$ facet. consistent with the SIMS data. The EL output power is low with a too low $Cp_2Mg/TMGa$ of 0.04% due to the inferior hole injection efficiency and stays almost constant with $Cp_2Mq/TMGa$ ranging from 0.06% until 0.21% for the 3D LEDs with the {1011} facet. Since Hall measurement is not applicable and SIMS is difficult on 3D structures, the good range of the hole conductivity for high EL output power could be recorgnized by the line shape of the Mg DAP band. Heavy Mg doping in the p-GaN capping layer is required to achieve good ohmic contact performance.

1. Introduction

High power InGaN/GaN based green light emitting diodes (LEDs) attract worldwide interest nowadays. However, the efficiency of the InGaN/GaN QWs decreases drastically with increasing emission wavelength. On one hand, this is attributed to the degraded material quality with increasing indium content [1]. On the other hand, owing to the polar character of the nitride semiconductors, the increasing strain in such QWs leads to huge internal electric fields resulting in a local separation of electrons and holes and hence reducing their recombination probability. Consequently, many groups are making efforts to fabricate semipolar/nonpolar InGaN/GaN QW structures following different approaches [2,3]. Previously, we have demonstrated high quality semipolar LEDs grown on the side-facets of three-dimensional (3D) structures fabricated by selective area growth (SAG) on c-plane sapphire. This approach yields high material quality and is compatible with large scale production on full 2 inch or even larger wafers [4].

Good p-type GaN conductivity is important to obtain effcient InGaN/GaN LEDs. The ptype conductivity of metalorganic vapor phase epitaxy (MOVPE) grown GaN is achieved by Mg doping following low energy electron irradiation [5] or thermal annealing [6]. The hole concentration is limited to about 2×10^{18} cm⁻³ by self-compensation leading to low hole conductivity [7]. Lots of investigations were done for the optimal hole conductivity of c-plane and planar semipolar p-GaN. However, little is known about the 3D semipolar p-GaN since Hall measurement is not applicable and SIMS is difficult on 3D structures. This paper reports the determination of the Mg concentration of 3D semipolar p-GaN $- \{10\overline{1}1\}$ and $\{11\overline{2}2\}$ – via secondary ion mass spectrometry (SIMS) analysis. The line shape of the donor-acceptor-pair (DAP) luminescence measured by low-temperature µphotoluminescence (LT µ-PL) can be correlated to the hole conductivity qualitatively. Moreover, we worked on optimizing the contact resistivity to our p-doped layers by heavy Mg doping in the p-GaN capping layer in order to achieve an ohmic contact performance.

2. Experimental

Epitaxial growth was carried out in a low pressure MOVPE horizontal reactor using TMGa, TEGa, TMIn, TMAl, Cp_2Mg , SiH_4 and NH_3 as precursors. Firstly, a $3\mu m$ thick high quality GaN layer was grown on c-plane sapphire employing a SiN nanomask layer for defect density reduction [8]. Then, a $200 \,\mathrm{nm}$ thick SiO₂ layer was deposited on the GaN template by plasma enhanced chemical vapor deposition (PECVD) and removed completely within one quarter of the wafer, patterned into periodic stripes with 10 µm wide masked area and 3 µm wide opening along the crystal directions $\langle 11\bar{2}0 \rangle$ and $\langle 10\overline{1}0 \rangle$, respectively, within another two quarters of the wafer and patterned into periodic hexagons within the fourth quarter of the wafer via photolithography and dry etching. The structure formed with the epi-mask of the hexagonal pattern is not discussed in this paper. Finally, epitaxial overgrowth was applied on the processed template: On the two quarters of the wafer with the stripe pattern, 3D Si-doped GaN stripes with triangular cross-section and a height of about $8.5\,\mu\mathrm{m}$ were formed. On the semipolar side facets of these stripes, 5 InGaN/GaN quantum wells, a 5 nm thick undoped GaN spacer, 250 nm thick Mg-doped GaN and a thin heavily doped p-GaN capping layer were deposited sequentially to form the complete LED structure. Meanwhile, a c-plane LED structure was grown on the quarter of the wafer without any SiO_2 epi-mask in the same epitaxial run. Following growth, the wafers were annealed in an air atmosphere at 750 °C for 1 min in order to depassivate the Mg acceptors. Imaging SIMS is required to characterize the material composition from an inhomogeneous surface which obviously is the case for the stripe LEDs. The Mg depth profile was measured by imaging SIMS using a finely focused primary ion beam to achieve a lateral resolution of about 150 nm. The sputtering ion beam was oriented in parallel with the GaN-based stripes and with an angle of 45° to the sample surface for the two types of stripe LEDs. The EL measurements were done on-wafer with evaporated indium contacts. More details about the fabrication procedure can be found elsewhere [4].



Fig. 1: The SIMS signals of the Si (left), Mg (middle) and In (right) ions integrated over a sputtering depth of $1-2 \,\mu\text{m}$ for the stripe LED with the $\{11\overline{2}2\}$ facet (Cp₂Mg/TMGa = 0.06 %).

3. Results

The chemical Si, Mg and In concentrations of the sample with a molar flow ratio between Cp_2Mg and TMGa ($Cp_2Mg/TMGa$) of 0.06% during the main p-GaN layer growth were determined by imaging SIMS for the three different structures, c-plane LED and stripe LEDs with the {1011} and {1122} facets, respectively. The Si, Mg and In signals integrated over a sputtering depth of 1–2 µm are shown in Fig. 1 for the stripe LED with the {1122} facet indicating the expected stripe period of 13 µm. Obviously the area with a high Si concentration is the SiO₂ epi-mask between the GaN-based stripes. Within the same area, high Mg and In concentrations are detected, presumably as an artifact of the SIMS measurement. The coexistence of the element Si typically enhances the detected signal intensity of other elements in SIMS measurements. At the stripe tip, a low In concentration is detected opposite to the reported increasing In concentration from the bottom to the tip of the stripes [4]. This is presumably due to the different sputtering behavior there.

The Mg concentration was determined for the stripe LEDs from a rectangular integration area with the size of $1.5 \times 40 \,\mu\text{m}^2$. The integration window was positioned with the long side parallel to the stripes and in the middle of the stripe facet to avoid the measurement artifacets caused by the SiO₂ epi-mask and the stripe tip. The Mg concentrations in the main p-GaN layer of the stripe LEDs with the $\{10\bar{1}1\}$ and $\{11\bar{2}2\}$ facets and the c-plane LED are $4 \times 10^{19} \,\text{cm}^{-3}$, $1.5 \times 10^{19} \,\text{cm}^{-3}$ and $1.5 \times 10^{19} \,\text{cm}^{-3}$, respectively, for the single wafer with Cp₂Mg/TMGa = 0.06 % (Fig. 2). Hence, the Mg incorporation efficiency on the GaN crystal plane $\{10\bar{1}1\}$ is higher than that on $\{11\bar{2}2\}$. The Mg incorporation efficiency is not directly comparable between the planar c-plane and the 3D semipolar structures due to the different surface morphologies.

In order to study the influence of the Mg concentration on the EL performance of the stripe LED with the {1011} facet, Cp₂Mg/TMGa was chosen to be 0.04%, 0.06%, 0.10%, 0.15% and 0.21% during the main p-GaN layer growth for five samples (samples #1-5). The Mg concentration is expected to depend on the Cp₂Mg/TMGa linearly [9]. The Mg concentrations of samples #1 and #3–5 are estimated to be $3 \times 10^{19} \text{ cm}^{-3}$, $7 \times 10^{19} \text{ cm}^{-3}$, $9 \times 10^{19} \text{ cm}^{-3}$ and $1.3 \times 10^{20} \text{ cm}^{-3}$ based on the Mg concentration of $4 \times 10^{19} \text{ cm}^{-3}$ for sample #2 characterized by imaging SIMS. In order to relate the Mg concentration qualitatively





Fig. 2: The SIMS depth profile of the Ga, Mg and In concentrations for the stripe LEDs with the $\{10\overline{1}1\}$ (a) and $\{11\overline{2}2\}$ (b) facets and the c-plane LED (c) at the same growth conditions (Cp₂Mg/TMGa = 0.06 %).

to the PL spectrum, LT µ-PL was applied by employing a He-Cd laser $\lambda = 325$ nm as the excitation source. The excited area is around the stripe tip with a diameter of 1– 2µm. As shown in Fig. 3, pronounced donor-acceptor-pair (DAP) luminescence at 3.24 eV with characteristic LO-replicas was observed with Cp₂Mg/TMGa of 0.04% and 0.06%. With further increasing Cp₂Mg/TMGa of 0.10% and 0.21%, the DAP band shifts to a broad band emission at a lower energy presenting the emergence of self-compensation via the MgV_N pair [7,10] for the stripe LEDs with the {1011} facet. In contrary, selfcompensation was not observed up to Cp₂Mg/TMGa of 0.21% for the stripe LEDs with the {1122} facet. Thus, the Mg incorporation efficiency on the {1011} facet is concluded to be higher than that on the {1122} facet, consistent with the SIMS data.

EL is measured for all the five stripe LEDs with the $\{10\overline{1}1\}$ facet. The EL output power is low with a too low Mg concentration of 3×10^{19} cm⁻³, probably due to the inferior hole injection efficiency, and stays almost constant with Mg concentration ranging from 4.0×10^{19} cm⁻³ to 1.3×10^{20} cm⁻³ for the 3D LEDs with the $\{10\overline{1}1\}$ facet (Fig. 4). Obviously, it is not critical to control the Mg doping concentration very accurately to achieve high EL output power. A Mg doping concentration window between 4.0×10^{19} cm⁻³ and 1.3×10^{20} cm⁻³ could offer good enough hole conductivity aiming at high EL output power. The Mg-related DAP emission shifts from a peak at 3.24 eV with the characteristic LOreplicas to the broad band at a lower energy during the suitable Mg doping concentration window as discussed above. These results show, that the typical change of the line shape of the Mg-related emission allows to recognize a suitable Mg doping concentration for 3D structures.



Fig. 3: The LT μ -PL spectra of the stripe LEDs with the {1011} (left) and {1122} (right) facets varying Cp₂Mg/TMGa during the main p-GaN layer growth. The spectra is normalized to the intensity of the GaN D^OX peak. The excited area is around the stripe tip with a diameter of 1–2 µm.

In order to obtain good ohmic p-contact performance, Cp₂Mg/TMGa was ramped up from 0.06% for the main p-GaN layer growth to 0.80%, 1.34% and 1.60% during the growth of a thin p-GaN capping layer for three samples. The Mg concentration at the sample surface, in other words, at the interface between the p-type semiconductor and the metal contact, was measured to be about 2×10^{20} cm⁻³ for the second sample by SIMS. With a linear extrapolation, the Mg concentration at the sample surface is estimated to be 1.2×10^{20} cm⁻³ and 2.4×10^{20} cm⁻³ for the first and third samples.

The complete LED device can be modelled as a Schottky diode and a pn-diode connected in series if there is any Schottky barriers between the p-type semiconductor and the metal contact. The relation between the voltage V and the current I is expressed by the equation:

$$V = \sum \frac{n_i kT}{q} \ln\left(\frac{I+I_{\rm si}}{I}\right), i = 1, 2.$$
(1)

n, k, T, q and I_s represent the ideality factor, Boltzmann's constant, the absolute temperature, the elemental charge and the saturation current of the diode, respectively. Two items with i = 1, 2 stand for the voltage over the pn junction and the Schottky barrier at the p-type contact. Hence, the knee voltage of the complete device is the summation of the knee voltages of the pn junction and the Schottky barrier between the p-type semiconductor and the metal contact.



Fig. 4: The EL output power of the stripe LEDs with the $\{10\overline{1}1\}$ facet varying Cp₂Mg/TMGa during the main p-GaN layer growth.

The knee voltage of the LEDs with the $\{10\overline{1}1\}$ facet is determined from their IV curves (Fig. 5 (left)). It drops from 6.3 V to 4.3 V by increasing the Mg concentration from $1.2 \times 10^{20} \text{ cm}^{-3}$ to $2.0 \times 10^{20} \text{ cm}^{-3}$ and rises to 5.0 V with an even higher Mg concentration of $2.4 \times 10^{20} \text{ cm}^{-3}$. Excessive Mg doping is required to produce a deep-level-defect (DLD) band in the p-GaN capping layer and the carriers are transported from the metal contact to the p-GaN capping layer through the DLD band instead of overcoming a Schottky barrier [11]. The low Mg doping level of $1.2 \times 10^{20} \text{ cm}^{-3}$ results in a Schottky barrier between the semiconductor and the metal contact leading to a high knee voltage. The contact resistance is also higher in this case indicated by the slope of the IV curve after the diode switch-on compared to the other two samples with larger Mg concentrations. Thus, heat is generated due to the poor contact performance during the EL leading to a high junction temperature. As a result, the diode breaks down at a small operating current of 85 mA (Fig. 5 (right)) and the emission efficiency is lower when operated with a cw current compared to a pulsed current (Fig. 6).



Fig. 5: The IV curve (left) and the output power (right) of the stripe LED with the $\{10\overline{1}1\}$ facet varying the Mg concentration at the interface between the p-type semiconductor and the metal contact.



Fig. 6: The EL output power of the stripe LED with the $\{10\overline{1}1\}$ facet and the Mg concentration of 1.2×10^{20} cm⁻³ at the interface between the p-GaN and the contact metal under cw and pulsed currents.

The contact performance is improved by heavier Mg doping with the Mg concentration of 2×10^{20} cm⁻³ and deteriorates again slightly with an even higher Mg concentration of 2.4×10^{20} cm⁻³, presumably due to the crystal quality degradation with a too high Mg doping level.

Table 1: The knee voltage of the stripe LED with the $\{10\overline{1}1\}$ facet varying the Mg concentration at the interface between the p-type semiconductor and the metal contact.

Mg concentration (cm^{-3})	1.2×10^{20}	2×10^{20}	2.4×10^{20}
knee voltage (V)	6.3	4.3	5.0

4. Summary

Secondary ion mass spectrometry analysis revealed the Mg concentration of the 3D semipolar p-GaN, indicating a higher Mg doping concentration on the $\{10\overline{1}1\}$ facet by a factor of 2.7 compared to the $\{11\overline{2}2\}$ facet under the same growth conditions. The line shape of the Mg-related donor-acceptor-pair (DAP) emission confirmed the same conclusion that the Mg incorporation efficiency is higher on the $\{10\overline{1}1\}$ facet than on the $\{11\overline{2}2\}$ facet. The good range of the hole concentration for high EL output power could be estimated from the line shape of the Mg DAP band as well. The p-type contact performance was improved by excessive Mg doping.

Acknowledgment

I gratefully acknowledge the scientific and technical support from Y. Gao (Evans Analytical Group, USA), S. Bauer (Inst. of Quantum Matter), S. Alam and I. Schwaiger (Inst. of Optoelectronics). This work has been financially supported by the German Federal Ministry of Education and Research (BMBF).

References

- T. Langer, A. Kruse, F.A. Ketzer, A. Schwiegel, L. Hoffmann, H. Jönen, H. Bremers, U. Rossow, and A. Hangleiter, "Origin of the green gap: increasing nonradiative recombination in indium-rich GaInN/GaN quantum well structures", *Phys. Status Solidi C*, vol. 8, pp. 2170–2172, 2011.
- [2] K. Fujito, K. Kiyomi, T. Mochizuki, H. Oota, H. Namita, S. Nagao, and I. Fujimura, "High-quality nonpolar m-plane GaN substrates grown by HVPE", *Phys. Status Solidi A*, vol. 205, pp. 1056–1059, 2008.
- [3] F. Scholz, "Semipolar GaN grown on foreign substrates: a review", Semicond. Sci. Technol., vol. 27, pp. 024002-1–15, 2012.
- [4] T. Wunderer et al., "Three-dimensional GaN for semipolar light emitters", Phys. Status Solidi B, vol. 248, pp. 549–560, 2011.
- [5] H. Amano, M. Kito, K. Hiramatsu, and I. Akasaki, "P-type conduction in Mg-doped GaN treated with low-energy electron beam irradiation (LEEBI)", Jpn. J. Appl. Phys., vol. 28, pp. L2112–L2114, 1989.
- [6] S. Nakamura, T. Mukai, M. Senoh, and N. Iwasa, "Thermal annealing effects on p-type Mg-doped GaN films", Jpn. J. Appl. Phys., vol. 31, pp. L139–L142, 1992.
- [7] U. Kaufmann, P. Schlotter, H. Obloh, K. Köhler, and M. Maier, "Hole conductivity and compensation in epitaxial GaN:Mg layers", *Phys. Rev. B*, vol. 62, pp. 10867– 10872, 2000.
- [8] J. Hertkorn, F. Lipski, P. Brückner, T. Wunderer, S.B. Thapa, F. Scholz, A. Chuvilin, U. Kaiser, M. Beer, and J. Zweck, "Process optimization for the effective reduction of threading dislocations in MOVPE grown GaN using in situ deposited SiN_x masks", J. Cryst. Growth, vol. 310, pp. 4867–4870, 2008.
- [9] H. Amano, M. Kitoh, K. Hiramatsu, and I. Akasaki, "Growth and luminescence properties of Mg-doped GaN prepared by MOVPE", J. Electrochem. Soc., vol. 137, pp. 1639–1641, 1990.
- [10] L. Eckey, U.V. Gfug, J. Holst, A. Hoffmann, B. Schineller, K. Heime, M. Heuken, O. Schön, and R. Beccard, "Compensation effects in Mg-doped GaN epilayers", J. Cryst. Growth, vol. 189/190, pp. 523–527, 1998.
- [11] L.L. Wu, D.G. Zhao, D.S. Jiang, P. Chen, L.C. Le, L. Li, Z.S. Liu, S.M. Zhang, J.J. Zhu, H. Wang, B.S. Zhang, and H. Yang, "Effects of thin heavily Mg-doped GaN capping layer on ohmic contact formation of p-type GaN", *Semicond. Sci. Technol.*, vol. 28, pp. 105020-1–5, 2013.