

Photoluminescence studies of Mg-doped gallium nitride films grown by metalorganic chemical vapor deposition

Guarneros C. *

Posgrado en Física Aplicada, Facultad de Ciencias Físico-Matemáticas
Benemérita Universidad Autónoma de Puebla
Puebla, Pue., México

Sánchez V.

Departamento de Ingeniería Eléctrica, Sección de Electrónica del Estado Sólido
Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional
México D.F., México

(Recibido: 13 de diciembre de 2011; Aceptado: 03 de octubre de 2012)

Mg-doped GaN epitaxial layers grown by metalorganic chemical vapor deposition (MOCVD) have been investigated by Photoluminescence, Raman scattering and X-ray Diffraction in the as-grown condition and after annealing. The photoluminescence measurement showed 2.9 eV band associated with the optical transitions from the conduction band to the Mg acceptor. Raman spectra shows local vibrational modes at 647.73 cm^{-1} and 265 cm^{-1} related to a local vibrational mode (LVM) of magnesium in GaN and as evidence of p-type character, respectively. The XRD analysis was employed to study the structure of the films.

Keywords: Mg-doped GaN; Photoluminescence; Raman scattering; X-ray Diffraction Annealing

1. Introduction

GaN is employed as one of the most advantageous materials forming optical devices and electronic devices. The realization of high conducting p-type GaN films is one of the key factors to the success of GaN based light emitting devices such as light emitting diodes (LEDs) and laser diodes with low series resistance and high external quantum efficiency [2]. Magnesium is the commonly used impurity for p-type doping of gallium nitride and it can be introduced into the lattice during chemical vapor deposition (CVD). However, growth techniques such as metalorganic chemical vapor deposition (MOCVD) introduce large concentrations of hydrogen into the growing material. In p-type material, hydrogen behaves as a donor and forms neutral $(\text{Mg-H})^{\circ}$ complexes with acceptors suppressing the formation of self-compensating native point defects (e. g. V_{N}) [3]. Therefore, post-growth annealing is required in order to activate those acceptors [4]. These processes are either low energy electron beam irradiation (LEEBI) or a N_2 -ambient thermal annealing above 600°C . The activation process involves the dissociation of acceptor-hydrogen complexes rather than the removal of separate compensating donors [5].

Depending on the growth conditions and the magnesium concentration various types of emission are observed in GaN:Mg. For light Mg doping (Mg concentration 10^{17} - 10^{18} atom/cm^3) and at low temperatures, the set of bands at about 3.27 eV with 92 meV LO-phonon replicas is observed. These are related to the bound exciton associated with the decay of exciton bound at neutral acceptor sites

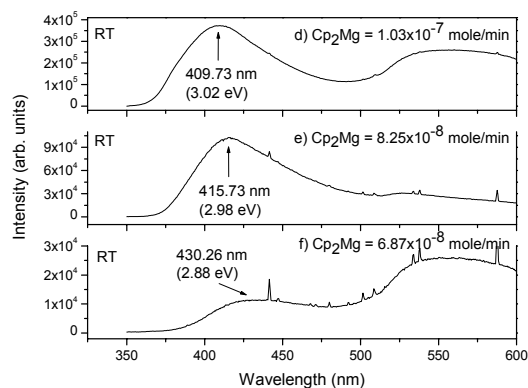


Figure 1. Photoluminescence spectra measured at room temperature of GaN:Mg epilayers growth with different Cp_2Mg flow rates.

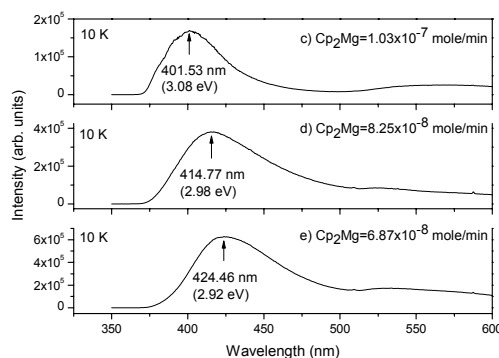


Figure 2. Low temperature (10 K) photoluminescence spectra of unannealed GaN:Mg epilayers growth with different Cp_2Mg flow rates.

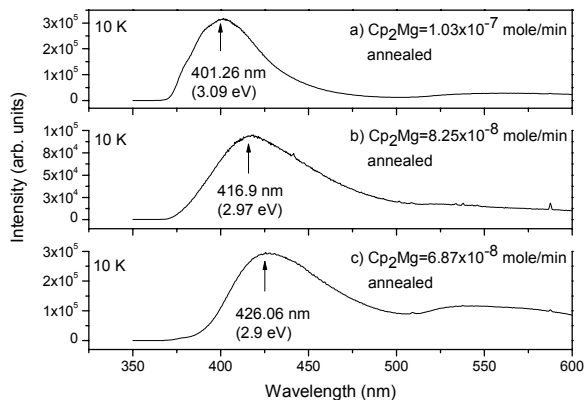


Figure 3. Low temperature (10 K) photoluminescence spectra of annealed GaN:Mg epilayers growth with different Cp₂Mg flow rates.

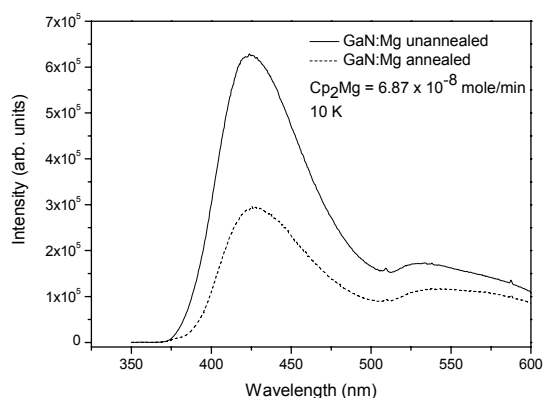


Figure 4. Comparison of the photoluminescence spectra between the unannealed and annealed GaN:Mg sample.

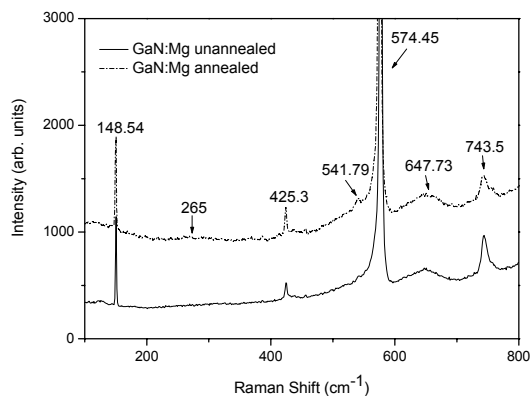


Figure 5. Raman spectra of GaN:Mg layer before thermal treatment and after thermal treatment when the Cp₂Mg flow rate is equal to 6.87x10⁻⁸ mole/minute.

and donor-acceptor pair (DAP) emission due to optical transitions from shallow donor to a shallow Mg acceptor.

For heavier magnesium doping, which is required to obtain p-type material (Mg concentration 10¹⁹ atom/cm³), samples often exhibit an ultraviolet band at 3.1 eV – 3.2 eV, which can overlap with 3.27 eV DAP emission. Moreover, quite often a strong blue luminescence band at 2.7 eV – 2.9 eV is observed in conjunction with 3.1 eV band or completely dominates the spectrum. The former is due to the optical transitions from the conduction band to the Mg acceptor. And the latter is attributed to transitions from the conduction band to a deep acceptor level or to Mg complex [1, 5].

In order to investigate magnesium doping characteristics in GaN, several kinds of GaN films were grown varying the flow rate of Cp₂Mg dopant.

2. Methodology

P-type GaN:Mg layers were deposited on (0001) oriented (Al₂O₃) sapphire substrates using low pressure MOCVD horizontal quartz reactor [6]. The heater around the quartz reactor was composed of seven infrared lamps; the electrical power per lamp was 1600 W. Prior to loading into the reactor the Al₂O₃ substrates were cleaned ultrasonically in organic solvents then chemically etched in a hot H₃PO₄:H₂SO₄ (1:3) solution for 10 minutes and finally rinsed in de-ionized water.

A low temperature GaN buffer layer (520° C) was grown using trimethylgallium (TMGa) and ammonia (NH₃) as Ga and N precursors, respectively. After deposition of the GaN buffer layer, the substrate temperature was raised to 900° C to grow GaN epitaxial layer. During the growth of the buffer layer and main layer, TMGa flow rate was varied to 6.23x10⁻⁶ mole/min, 4.99x10⁻⁶ mole/min and 4.13x10⁻⁶ mole/min, NH₃ kept the flow rate to 5 slm. Bis-(cyclopentadienyl)magnesium (Cp₂Mg) was used as p-type doping source with different flow rates, 1.03x10⁻⁷ mole/min, 8.25x10⁻⁸ mole/min and 6.87x10⁻⁸ mole/min. The layers of p-GaN were grown at 900° C for 60 minutes. H₂ was used as carrier gas with a flow rate to 4 slm, 5 slm and 6 slm. The reactor pressure was kept at 76 Torr. The GaN:Mg layers were annealed in a nitrogen ambient for 30 minutes at 750° C.

3. Results and Discussion

PL measurements were performed at room temperature and for the low temperature measurements the samples were mounted in a cryostat to achieve a sample temperature of 10 K. The PL spectra were excited with 325 nm line of 10 mW He-Cd laser. The spectra were collected with a double-grating monochromator and recorded with a photomultiplier tube. X-ray diffraction measurements were obtained using an X-Ray Diffractometer D5000 Siemens with Cu target operated at 35 kV and 25 mA.

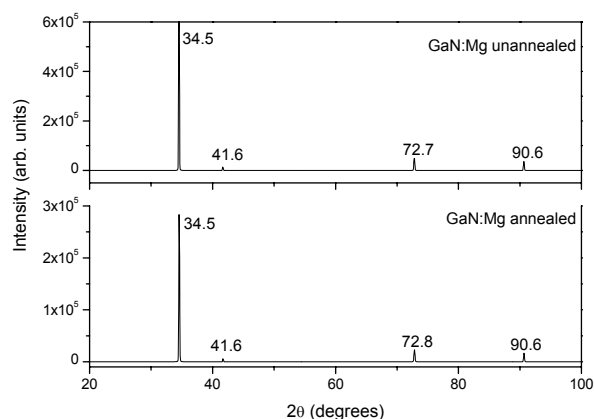


Figure 6. X-ray diffraction pattern of GaN:Mg layer before thermal treatment and after thermal treatment.

Fig. 1 shows a typical Mg characteristic of PL spectrum on p-GaN measured at room temperature. The PL measurement shows broad Mg-related emissions at 409.73 nm (3.02 eV), 415.73 nm (2.98 eV) and 430.26 nm (2.88 eV), lead to the conclusion that deep, compensating centers are associated with the Mg incorporation into GaN.

Low temperature (10 K) photoluminescence spectra of GaN epilayers with different Cp_2Mg flow rates are shown in Fig. 2. The emission bands centered at 401.53 nm (3.08 eV), 414.77 nm (2.98 eV) and 424.46 nm (2.92 eV) are probably associated with a transition between a deep localized donor and an acceptor (likely the magnesium-related acceptor state) [7]. After annealing of these samples, significant changes are not observed in the intensity of the PL lines at 10 K, it is observed small displacements at 401.26 nm (3.09 eV), 416.9 nm (2.97 eV), and 426.06 nm (2.9 eV) (Fig. 3). The Fig. 4 is a comparison between to the unannealed and annealed sample; it is observed that the intensity of blue emission decreases with the thermal annealing at 750° C. Therefore, this temperature dependence of the blue emissions indicates that the intensity change is not only related to the p-type conduction mechanism but also to other crystal qualities of Mg-doped GaN films. It is possible that the decrease in the intensity of blue emissions was caused by the thermal dissociation of GaN since the dissociation pressure of GaN gradually increases above 700° C [8].

Raman spectra were observed at room temperature using a He-Ne laser at 632.8 nm for the excitation source. Fig. 5 shows Raman spectra when the Cp_2Mg flow rate is equal to 6.87×10^{-8} mole/min. The top spectrum was obtained from annealed sample, while the bottom one is from pre-anneal sample. The sharp common peaks are ascribed to phonon modes of GaN, E_2 (148.54, 574.45 cm^{-1}) and A_1 (LO, 743.5 cm^{-1}), and a sapphire substrate signal (425.3 cm^{-1}). When the sample is annealed new features appear: Local Vibrational Modes appear at 647.73 and 265 cm^{-1} upon annealing at above 750° C. According to H. Harima, the 647.73 cm^{-1} peak is assigned to the LVM for the Mg (activated)-N bond, because a) the frequency agrees with

an estimate from the optical mode frequency of GaN (541.79 cm^{-1}), obtained by considering the difference in reduced mass between the Mg-N and Ga-N pairs; and b) the mode intensity is almost proportional to the hole density. The other peak at 265 cm^{-1} that appeared upon annealing probably has the same origin [9].

X-ray diffraction pattern of p-GaN layer grown on sapphire substrate measured before and after thermal treatment is shown Fig. 6. The peak at 34.5° and 72.7° along the (0002) and (0004) planes, respectively, correspond to GaN with wurtzite structure; it means that the p-GaN layer is epitaxially crystallized even though the lattice mismatch between GaN and Al_2O_3 is very large. Also, this indicates that the grown layer is strongly oriented to the c-axis of hexagonal structure with (0002) preferential orientation. The peaks at 41.6° and 90.6° correspond to sapphire substrate. When the sample was annealed the intensity of the (0002) peak diffraction decreases may due to the thermal dissociation of GaN.

4. Conclusions

The PL measurements at low temperature showed a strong blue luminescence band with the peak position centered from 2.9 eV. Raman spectra shows local vibration modes at 647.7 cm^{-1} and 265 cm^{-1} related to a local vibration mode of magnesium in GaN and as evidence of p-type character, respectively. The XRD analyses indicate that the grown layer is strongly oriented to the c-axis of hexagonal structure with (0002) preferential orientation. When the samples were annealed significant changes are observed, the blue emission decreases so there is no need a thermal annealing for magnesium acceptor activation. This is of great importance for the devices elaboration, since it would avoid an additional technological step.

References

- [1] Y. Nakagawa, M. Haraguchi, M. Fukui, S. Takanaka, A. Sakaki, K. Kususe, N. Hosokawa, T. Takehara, Y. Morioka, H. Iijima, M. Kubota, M. Abe, T. Mukai, H. Takagi and G. Shinomiya, *Jpn. J. Appl. Phys.*, **43**, 23 (2004).
- [2] K. S. Kim, G. M. Yang, H. J. Lee, *Solid-State Electronics*, **43** 1807 (1999).
- [3] O. Gelhausen, H. N. Klein, M. R. Phillips, *Appl. Phys. Lett.*, **81** 3747(2002).
- [4] C. G. Van de Walle, *Phys. Rev. B*, **56** R10020(1997).
- [5] W. Götz, N. M. Johnson, J. Walker, D. P. Bour, and R. A. Street, *Appl. Phys. Lett.*, **68** 667(1996).
- [6] V. M. Sánchez Reséndiz, *Crecimiento y caracterización de heteroestructuras: GaAs sobre Si*, Tesis Doctorado CINVESTAV-IPN (Sección de Electrónica del Estado Sólido) México D. F. 2000.
- [7] T. S. Jeong, C. J. Youn, M. S. Han, J. W. Yang, K. Y. Lim, *J. Cryst. Growth.*, **259**, 267 (2003).
- [8] H. Teisseyre, T. Suski, P. Perlin, I. Grzegory, M. Leszczynski, M. Bockowski, and S. Porowski, *Phys. Rev B*, **62** 10151(2000).
- [9] S. Nakamura, T. Mukai, M. Senoh and N. Iwasa, *Jpn. J. Appl. Phys.*, **31** L139 (1992).
- [10] H. Harima, *J. Phys.: Condens. Matter*. **14** R967 (2002).