Passivation of yellow luminescence defects in GaN film by annealing and CF$_4$ plasma treatment

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In this study, we demonstrated that yellow luminescence (YL) defects can be mitigated with proper annealing or CF$_4$ plasma treatment. Multiple material analyses, including X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and surface roughness measurements were performed to investigate improvements in GaN film material properties caused by annealing and CF$_4$ plasma treatment. Filling vacancies during the annealing process and incorporating fluorine atoms to bond with dangling bonds during the plasma treatment process may lessen YL defects and decrease YL luminescence.

1. Introduction

Performance of GaN based optoelectronic and electronic devices has made remarkable progress over the past years. After S. Nakamura et al. [1] introduced the first GaN blue LED, high-performance and full-color semiconductor lighting incorporated GaN optoelectronic devices have been commercialized. Besides, the first AlGaN/GaN HEMT was demonstrated in 1993 [2] as a promising candidate among many electronic device technologies for high power applications. However, defects induced by material growth and device fabrication can cloud the promise for future development. Among various defects in GaN materials, yellow band luminescence peaking around 2.3 eV is the most famous broad band luminescence in GaN material [4]. Since 1980, many studies have been conducted on yellow band luminescence. The YL defect has been observed both in GaN LEDs [5] and GaN electronic devices [6], and has been shown to raise reliability concerns [7]. Therefore, passivation of this defect is necessary to improve GaN material quality and elevate device reliability. However, passivating YL defects in GaN film has not been clearly reported until now [8]. In this study, we demonstrate that YL defects can be mitigated through proper annealing or plasma treatment. In addition, multiple material analyses are performed to gain insight into the conditions under which improvements in YL defects occurred.

2. Experimental

To investigate the properties of YL defects in GaN film, a layer of c-plane (0001) GaN thin film of 1 μm in thickness was deposited by MOCVD on a 100 μm-thick sapphire substrate. To compare the as-deposited sample with the samples treated by annealing or plasma reaction, two samples were post-annealed by rapid thermal annealing for 30 s in an N$_2$ ambient at 200°C and 400°C, and three other samples were treated with CF4 plasma using RF power of 50W, 100W, and 250W for 3 min to improve film quality. Photoluminescence spectra of samples excited with a 300 nm wavelength argon laser were collected using a spectrometer to analyze defect variations. To study the conditions under which improvements in the defects occurred, samples were treated at different annealing temperatures and plasma treatment conditions, and were examined by various material analyses, including X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), and surface roughness measurements.

3. Results and discussion

To study the YL characteristics of GaN films, PL spectra of different samples were measured by exiting an argon laser, as shown in Fig. 1. The highest peak, at a spectra of around 370 nm - 380 nm, represents the GaN band-edge emission, while the peak at around 520 nm represents the emission from the YL defect. Among the samples, the deposited sample had the highest YL peak. The YL intesity for the sample annealed at 200°C decreased, and YL intensity disappeared entirely from the sample annealed at 400°C. Similarly, YL luminescence could not be observed for samples treated with CF$_4$ plasma at various RF powers. In addtion, PL spectra of samples

treated at different RF powers showed slight differeces, so one spectrum of the plasma-treated sample is presented in Fig. 1. According to the PL measurements, CF_4 plasma treatment or annealing at a high temperature of 400°C effectively suppresses YL luminescence.
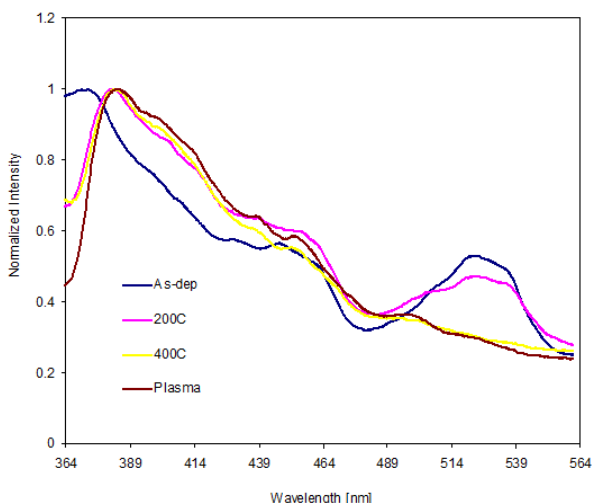

Fig. 1 PL spectra of GaN samples treated in different conditions

Table 1. Surface roughness values of GaN samples treated in different condtions

Treatments	As-dep	Annealing at 200℃	Annealing at 400℃	Plasma
Surface Roughness [nm]	34	32	28	28

Multiple material analyses were conducted to study the effects caused by plasma treatment or annealing, including surface roughness measurements, XRD, and XPS. To examine the surface roughness of the GaN film, 3D measuring laser microscope Olympus OLS 4000 examined the surfaces of the treated samples, with roughness values presented in Table 1. Changes in roughness values reveal material property improvements caused by annealing or CF_4 plasma treatment. As shown in Table 1, the surface roughness value of the as-deposited sample was 34 nm. The surface became smoother after annealing at 200°C, as the roughness value of the sample annealed lowered to 32 nm. As the annealing temperature further increased to 400°C, the GaN surface became smoother still, as the roughness value lowered to 28 nm. Similarly, the roughness of the plasma-treated sample was 28 nm. According to previous research [9], YL defects are related to Ga vacancies. Since annealing can fill in vacancies and eliminate dangling bonds, the surface of the

sample treated at 400°C demonstrates that high-temperature annealing treatment can mitigate defects and create a smoother surface. Similarly, CF_4 plasma treatment allows for the addition of fluroine atoms into the GaN film. These incorporated fluorine atoms can also bond with dangling bonds, decreasing the number of defects. Therefore, YL defects can be suppressed by either annealing or plasma treatment.
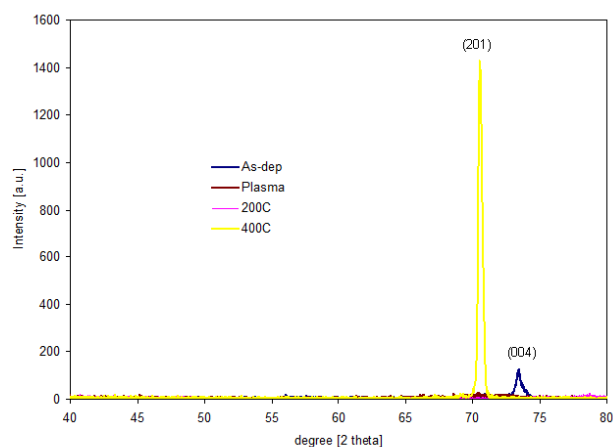

Fig. 2 XRD spectra of GaN samples treated in different condtions

Changes in GaN film crystalline structures induced by annealing and plasma treatment were further examined using XRD analysis. Samples treated uncer different conditions show various crystalline structures, as shown in the XRD spectra in Fig. 2. The as-deposited sample exhibits a strong peak around 73.5°, indicating the presence of a (400) oriented crystalline phase. After the samples treated with CF_4 plasma or annealing at 400°C, the (201) phase around 71° rose. Based on previous research [10], the removal of luminescence defects may favor certain directions in the crystalline phase, while luminescence defects may favor other directions. The (201) crystalline phase may be related to the removal of defect luminescence and the (400) oriented crystalline phase may favor YL luminescece in GaN film. In the XRD spectra, a strong (201) crystalline phase can be observed for the sample annealed at 400°C but a tiny (201) crystalline phase can be observed for the sample treated with CF_4 plasma. The removal of YL defects caused by high-temperature annealing is from the reflow of atoms in GaN film, while the removal of the defects caused by CF_4 plasma treatment is due to the incorporation of fluorine atoms [11]. Therefore, while the XRD spectra of the samples treated by high-temperature annealing and CF_4 plasma treatment show different characteristics, YL defects can be suppressed by either.
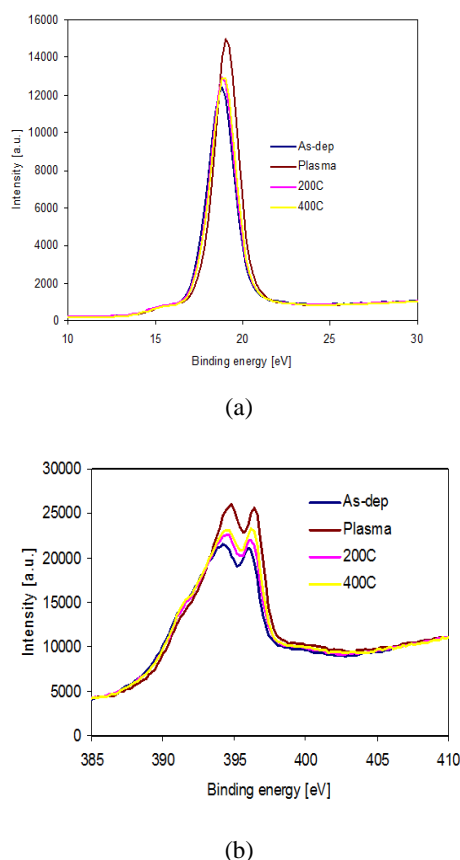
(a)

(b)

Fig. 3 (a) Ga 3d XPS spectra and (b) N 1s XPS spectra of GaN sample treated in different condtions.

Finally, to evaluate chemical binding status, XPS was used to measure the GaN film in different treatment conditions. Figure 3(a) shows the Ga 3d XPS spectra and Fig. 3(b) shows the N 1s XPS spectra [12]. In Fig. 3(a), a binding energy of 19 eV represents a well-bonded GaN chemical bonding status [13]. Annealing can increase the Ga 3d XPS peak intensity and binding energy, indicating the potential for stronger GaN bonds to form. As for the plasma-treated sample, the XPS peak intensity and the peak binding energy were increased even further. Since fluorine atoms can bond with dangling bonds, CF$_4$ plasma treatment can further reinfornce bond connections in GaN film. Similarly, in the N 1s spectra shown in Fig. 3(b), a two-peak (394eV and 396 eV doublet) profile represents a Ga-N bond. Annealing can also increase the N 1s XPS peak intensity and the peak binding energy, indicating the potential for formation of stronger GaN bonds. Furthermore, the plasma-treated sample had an even larger XPS peak intensity and energy, signifying the formation of stronger GaN bonds.

4. Conclusions

This study reports that YL defects can be effectively suppressed by high-temperature annealing and CF$_4$ plasma treatment. Through surface measurements, XRD and XPS analyses, vacancies being filled in during the annealing process and fluorine atoms bonding with dangling bonds during plasma treatment indicate that these treatments lead to improvements in YL defects. Given the promise for enhanced optoelectronic and electronic device applications shown by GaN, it is important to provide a clear understanding into the mechanisms behind the improvements caused by annealing and plasma treatment in order to enhance future improvements in GaN film processes.

References

[1] S. Nakamura, M. Senoh, N. Iwasa, S. Nagahama, Jpn. J. Appl. Phys. **34**, 797 (1995).
[2] A. Khan, A. Bhattarai, J. N. Kuznia, D. T. Olson, Appl. Phys. Lett. **63**, 1214 (1993).
[3] H. Chen, P. Preecha, Z. Lai, and G. P. Li, Journal of The Electrochemical Society, **155**, 648 (2008).
[4] T. Ogino and M. Aoki, Jpn. J. Appl. Phys, **19**, 2395 (1980).
[5] H. Chen, Z. Lai, S. C. Kung, R. M. Penner, Y. C. Chou, R. Lai, M. Wojtowicz, and G. P. Li, Jpn. J. Appl. Phys. 47, 3336 (2008)
[6] J. Kikawa, S. Yoshida, and Y. Itoh, Solid-state Electron, **47**, 523 (2003).
[7] A. Hinoki, Y. Hiroyama, T. Tsuchiya, T. Yamada, M. Iwami, K. Imada, J. Kikawa,T. Araki, A. Suzuki, Y. Nanish, Mater. Res. Soc. Symp. Proc. **892**, 14.1 (2006)
[8] Gon Namkoong, W. A. Doolittle, and A. S. Brown, J. Appl. Phys. **91** 2499 (2003).
[9] J. Neugebauer and C. G. Walle Appl. Phys. Lett. **69**, 503 (1996).
[10] B.J. Jin, S. Im, S.Y. Lee, Thin Solid Films **366**, 107 (2000).
[11] C. S. Lai, W. C. Wu, J. C. Wang, T. S. Chao, Jpn. J. App. Phys. **45**, 2893 (2006).
[12] R. V. Ghita, C. Negrila, A. S. Manea, C. Logofatu, M. Cernea, M. F. Lazarescu, J. Optoelectron. Adv. Mater. **5**, 859 (2003).
[13] J. F. Moulder, W. F. Stickle, P. E. Sobol, K. D. Bomben, Handbook of X-ray Photoelectron Spectroscopy, Physical Electronics, Inc., Eden Prairie, MN, 1995.

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