Nature of the 2.8-eV photoluminescence band in Si-doped GaN

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Investigation on the defect-related luminescence centered around 2.8 eV in Si-doped GaN epilayers is presented. It is found that the mechanism of this blue emission (BL) is quite different from that of the yellow luminescence (YL). By comparing the photoluminescence (PL) spectra obtained from either front-side or backside excitation and combining with the results of the BL and YL-related PL excitation and the secondary-ion-mass spectroscopy measurements, we propose that the 2.8-eV emission is the transition from the substitutional oxygen donor (O_N) level at 0.25 eV above the conduction band to the $V_{Ga}-O_N$ complex acceptor. The energy level of the $V_{Ga}-O_N$ complex is found to be at 0.8 eV above the valence-band edge which is consistent with the theoretical calculation. In addition, we show that the V_{Ga} defect plays a key role in the link between the time evolution of the YL and BL spectra in GaN samples.

I. INTRODUCTION

Up to now gallium nitride (GaN) and the related materials have been widely studied for their multiple applications such as the UV blue light-emitting diodes (LED's), laser diodes (LD's), short-wavelength optical detectors and high-power/high-temperature electronics.¹⁻⁴ In spite of the progress in the growth methods, certain basic material properties, even of simple GaN epitaxial layers, are still poorly understood. In particular, the spectra of the photoluminescence (PL) commonly reveal two bands peaked in the yellow range centered around 2.27 eV and the blue range centered around 2.8 eV at room temperature. The impurities and defects giving rise to the yellow luminescence (YL) and the blue luminescence (BL) have not been clearly identified. The mechanisms of the recombinations are still controversial. For instance, the yellow luminescence has been ascribed to several transition models. Ogino and Aoki⁵ proposed a transition between a shallow donor and a deep acceptorlike level. Glaser *et al.*⁶ proposed the model of a deep donor-shallow acceptor transition. Hofmann *et al.*⁷ proposed a shallow donor-deep donor transition, and so on. Moreover, the "blue" luminescence has been observed not only from Mg-doped GaN films^{8,9} but also from Si-doped and undoped ones.¹⁰⁻¹³ Recently, Toth *et al.*¹³ suggest that the involvement of oxygen and hydrogenated gallium vacancies dominates the blue band emission in *n*-type GaN. However, the convincing evidence for this model has not been reported.

In this paper, we focus on the blue band and its relation with the possible defects. We present the results of the PL, the PL excitation (PLE), and the secondary-ion-mass spectroscopy (SIMS) measurements in Si-doped GaN samples. We suggest that the microscopic nature of the deep defect giving rise to the YL comes from the Ga vacancy (V_{Ga}), while that of the BL originates from a transition between the substitutional O_N donor level^{14,15} above the conduction band and the $V_{Ga}-O_N$ complex^{16,17} deep level. In addition, we point out that the V_{Ga} defect plays a key role in the peculiar behavior of the time evolution of the YL and BL spectra.

II. EXPERIMENT

The Si-doped GaN films used here were grown by metal-organic chemical vapor deposition (MOCVD) on *c*-face sapphire substrates. A thin GaN buffer layer (500 Å) was deposited at 500 °C right before the epitaxial GaN (3 μm) grown at 1000 °C. The growth rate of 3 μm/h was employed. The flow rate of the diluted silane (SiH_4) was controlled to achieve carrier concentration of $1.06 \times 10^{18} \text{ cm}^{-3}$ measured by Hall measurement.^{18,19} For the photoluminescence measurements, the sample was excited from either the GaN side (frontside) or the sapphire side (backside) by a 50-mW He-Cd laser emitting at 325 nm. A 0.85-m monochromator, a photomultiplier tube, and standard lock-in technique were used to detect the signal. For the PL excitation (PLE) measurements, the sample was excited from the front side. A tungsten lamp dispersed by a monochromator was used as the photoexcitation light source. The optical signal was recorded by a photomultiplier tube using lock-in amplification. The secondary-ion-mass spectroscopy measurements were performed by a CAMECA IMS-4f double focusing ion microanalyzer configured for cesium primary ion bombardment.

III. RESULTS AND DISCUSSION

Figure 1 shows the room-temperature frontside and backside PL spectra of the Si-doped GaN epilayer sample. Both frontside and backside spectra show a near-band edge luminescence line (UV line) at 3.413 eV and a broad YL band centered around 2.27 eV. For the frontside PL spectrum, the full width at half maximum (FWHM) of the UV line is about 50 meV and several phonon replicas are found at the lower energy side. This indicates the good quality of the sample used here. The 3.413-eV peak can be assigned to the transition from Si donor level to the valence-band edge, because it has been shown that the Si donor level locates at about 27 meV below the conduction band.^{20,21} A broad band centered around 2.8 eV in the blue spectral region is observed which is prominent in the frontside PL spectrum. In addition, the periodic intensity modulation appearing in the YL and BL

FIG. 1. Room-temperature photoluminescence spectra of the Si-doped GaN epitaxial thin film. The frontside PL spectrum is excited from the GaN side (a) and the backside PL spectrum is excited from the sapphire side.

bands is attributed to the Fabry-Perot effect formed by the air-GaN and the GaN-sapphire interfaces.¹¹

In comparison of the intensity of the PL spectra, the backside PL spectrum shows not only the more intense YL intensity but also the weaker UV intensity. This phenomenon indicates that the luminescence of the YL band comes mainly from the interface between the epilayer and buffer layer^{22,23} and most of the intrinsic defects giving rise to the YL may exist in this region. And that the periodic intensity modulation becomes unobvious due to the poor quality of the interface is consistent with this observation. Moreover, the BL almost cannot be observed in the backside PL spectrum. This fact implies that the key defect responsible for the BL is different from the intrinsic defect for the YL band.

In order to explore the possible mechanisms for the yellow and the blue bands further, we have performed the PL excitation (PLE) of the YL and BL bands. Figure 2 shows the room-temperature PLE spectra for the YL-related main PL emission with the detection energies at: (a) 2.0, (b) 2.24, (c) 2.37, and (d) 2.5 eV. These PLE detection energies are

FIG. 2. PL excitation spectra of the yellow luminescence at room temperature. The spectra are shifted vertically for clarity. The detection energies are set at (a) 2.0, (b) 2.24, (c) 2.37, and (d) 2.5 eV. The inset shows the room-temperature PL spectrum and the arrows mark the respective detection energies.

FIG. 3. Room-temperature PL excitation spectra for the BL-related main PL emission monitored at (e) 2.75, (f) 2.77, (g) 2.845, and (h) 2.91 eV. Also, the spectra are shifted vertically for clarity. It shows that the peak position depends on the excitation energy. The inset shows the PL spectrum at room temperature and the arrows mark the respective detection energies.

set to be in and between the YL band centered at 2.27 eV as indicated in the inset in Fig. 2. For all of the detection energies, the main absorption of excitation energy reaches a maximum at 3.44 eV, i.e., the band gap of GaN at room temperature. We see that the main absorption peak does not change with the different detection energies. Through a detailed study on a series of *n*-type and *p*-type materials by different techniques such as photoluminescence, Raman scattering, and photoconductivity, we proposed that the YL emission arises from the transition between the Si donor level and the deep level at about 1.1 eV above the valence band.^{24–26} Furthermore, we pointed out that the most probable candidate responsible for the YL emission can be attributed to Ga vacancy which is consistent with the recent theoretical calculation.^{16,17} In this paper, we will only concentrate on the nature of the BL emission.

Figure 3 shows the room-temperature PLE spectra for the blue luminescence taken with the detection energies at: (e) 2.75, (f) 2.77, (g) 2.845, and (h) 2.91 eV. The corresponding main peaks of the PLE spectra are clearly seen at 3.54, 3.56, 3.66, 3.75 eV, respectively. Note that the peak energies of the BL-related PLE spectra are all higher than the band gap of GaN, even higher than the energies of the A, B, and C valence-band-related transitions.⁵ This characteristic implies that the transition of the BL emission involves the energy level above the conduction band edge of GaN. Recently, both the theoretical calculation and experimental work have shown that the oxygen donor level locates at about 0.25 eV above the conduction band of GaN.^{14,15} The transition from the valence band edge to this substitutional O_N level is centered around 3.69 eV which is in good agreement with our PLE measurements. Additional experimental evidence was given by Toth *et al.*¹³ in which they showed the role of oxygen in *n*-type GaN and suggested that the blue luminescence results from an unknown O_N -related transition. Besides, the theoretical calculation provided by Neugubaur and Van de Walle^{16,17} shows that the energy level of the $V_{Ga}-O_N$ complex is about 1.0 eV above the valence-band edge. Based on these results, we therefore propose that the BL emission originates from the transition between the substitutional O_N

FIG. 4. Transition model of the YL and the BL bands. The YL band is due to the radiative transition from the Si-donor level to the V_{Ga} acceptor and the BL emission is the transition from the O_N donor to the $V_{Ga}-O_N$ complex acceptor. All the level positions are inferred from the numbers and the band gap is 3.44 eV at room temperature.

donor level and the $V_{Ga}-O_N$ complex level as shown in Fig. 4. From our experimental data, we obtain that the $V_{Ga}-O_N$ complex level locates at about 0.8 eV above valence band, which is in good agreement with the theoretical calculation.^{16,17} Here, the substitutional O_N donor is suggested to be the key factor for the BL. It has been reported that oxygen is an omnipresent impurity in GaN material system and the oxygen can be incorporated in GaN crystals as common contaminant during growth or on the surface.^{14,27} Since the oxygen can substitute the N site and serve as a donor, the negatively V_{Ga} acceptor and the positively charged O_N donor can easily attract each other and form the $V_{Ga}-O_N$ complex. The coupling between the V_{Ga} and O_N species makes the transition from the O_N donor level to the $V_{Ga}-O_N$ complex acceptor as an efficient recombination channel. Thus the electrons, which are excited from the valence band to the O_N level, tend to recombine with the holes in the $V_{Ga}-O_N$ complex level and it generates a blue emission with energy about 2.8 eV. In addition, in Fig. 3, it is found that the main absorption peak changes with the detection energy. This fact is probably because the energy level of the $V_{Ga}-O_N$ complex defect depends on the environment of the O_N and V_{Ga} defect. The region with different environment associated with the O_N and V_{Ga} defects may cause in the fluctuation of the energy level. Thus each $V_{Ga}-O_N$ complex has its own absorption and transition energies. When the detection energy is fixed, one measures the transition of a particular $V_{Ga}-O_N$ complex. The shift of the absorption peak with the detection energy as observed in the PLE spectra therefore can be understood.

Another piece of evidence to support our proposed mechanism for the BL emission is the SIMS depth profile of oxygen. In Fig. 5, it shows that oxygen is present both in the regions of the sapphire substrate and surface. We clearly see that the surface oxygen atoms are abundant and diffuse into the epilayer with approximate 0.4- μm depth. These oxygen atoms can replace the nitrogen sites, act as donors, and form the $V_{Ga}-O_N$ complexes. Jones *et al.*²⁸ have shown that the $V_{Ga}-O_N$ complex would be more stable at the surface region. Based on these results, we therefore can understand that the BL emission is much stronger for the frontside excitation and almost no BL emission is observed for the backside excitation as shown in Fig. 1. In order to further confirm our proposed mechanism, we have measured the PL spectrum of the

FIG. 5. The SIMS profiles of oxygen, silicon, and Ga+N for the Si-doped GaN sample. The dashed lines divide the epilayer (3 μm), buffer layer (500 Å), and substrate regions for clarity.

sample after intentional oxidation, and found that the 2.8-eV emission is enhanced after oxidation result which is consistent with the recent report.^{13,29,30} In Ref. 29, It shows that the additional oxygen dopant in GaN:Zn leads to the 2.8-eV emission. This result clearly indicates that the blue emission is related to the incorporation of oxygen. Recently, Hshieh *et al.*³⁰ have performed the studies of the photoelectrochemical (PEC) etching in GaN samples. They observed the appearance of the blue luminescence in GaN sample after the 3.5-M boiled KOH post treatment for 30 min with UV power density of 290 mW/cm². Due to the creation of oxygen ions under UV illumination, they inferred that the origin responsible for the blue emission is a oxygen-related donor-acceptor pair (DAP) transition. Thus all these results support the correlation between the 2.8-eV PL band and the presence of O as proposed in this work. Note that from the SIMS measurements, Mg atoms do not exist in our sample. This fact implies that the mechanism of the BL emission mentioned here is therefore different from that of the Mg-related BL emission proposed in other papers.^{8,9}

Further evidence to support our proposed mechanism for the 2.8-eV emission can be obtained from a previous report.¹² For example, in Ref. 12, it shows that the PL intensity of the BL band decreases as that of the YL band increases in the time evolution of the PL measurement. This behavior still remains as a puzzle in the study of GaN material. However, according to our proposed mechanism, it can be easily understood. In our model, if we assume that the isolated V_{Ga} dissociates from the $V_{Ga}-O_N$ complex after the absorption of photon, the concentration of the V_{Ga} increases and that of the $V_{Ga}-O_N$ decreases. From the discussion above, we know that the YL emission involves the transition of V_{Ga} defect level and the BL emission is associated to the $V_{Ga}-O_N$ defect. Thus the changes in the concentrations of the V_{Ga} and the $V_{Ga}-O_N$ complex lead to the opposite trend in the time evolution of the BL and the YL bands. We point out here that the key of the link between the BL and the YL bands is the V_{Ga} defect.

IV. CONCLUSION

In conclusion, we reported an investigation on the origin of the 2.8-eV luminescence in *n*-type GaN. By comparing

the PL spectra between the frontside and backside excitation, it is found that most of the intrinsic defects, the V_{Ga} , giving rise to the YL emission are formed in the interface between the epilayer and buffer layer. Based on a detailed study of PL, PLE, and SIMS measurements, we propose that the BL emission is a transition from the substitutional O_N donor level located at 0.25 eV above the conduction-band edge to the $V_{Ga}-O_N$ complex. According to our proposed mechanism, the

dissociation of the $V_{Ga}-O_N$ complex can be used to resolve the puzzle in the time evolution of the YL and BL spectra.

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- ¹S. Nakamura, T. Mukai, and M. Senoh, Appl. Phys. Lett. **64**, 1687 (1994).
- ²S. Nakamura, M. Senoh, S. Nagahama, N. Jwasa, T. Tamada, T. Matsushita, H. Kiyoku, and Y. Sugimoto, Jpn. J. Appl. Phys., Part 2 **35**, L74 (1996).
- ³I. Akasaki, H. Amano, M. Kito, and K. Hiramatsu, J. Lumin. **48**, 666 (1991).
- ⁴H. Morkoc, S. Strite, G. B. Gao, M. E. Lin, B. Sverdlov, and M. Burns, J. Appl. Phys. **76**, 1363 (1994).
- ⁵T. Ogino and M. Aoki, Jpn. J. Appl. Phys. **19**, 2359 (1980).
- ⁶E. R. Glaser, T. A. Kennedy, K. Doverspike, L. B. Rowland, D. K. Gaskill, J. A. Freitas, Jr., M. Asif Khan, D. T. Olson, J. N. Kuznina, and D. K. Wickenden, Phys. Rev. B **51**, 13 326 (1995).
- ⁷D. M. Hofmann, D. Kovalev, G. Steude, B. K. Meyer, A. Hoffmann, L. Eckey, R. Heitz, T. Detchprom, H. Ammono, and I. Akasaki, Phys. Rev. B **52**, 16 702 (1995).
- ⁸U. Kaufmann, M. Kunzer, M. Maier, H. Obloh, A. Ramakrishnan, B. Santic, and P. Schlotter, Appl. Phys. Lett. **72**, 1326 (1998).
- ⁹U. Kaufmann, M. Kunzer, M. Maier, H. Obloh, A. Ramakrishnan, and B. Santic, Phys. Rev. B **59**, 5561 (1999).
- ¹⁰E. F. Schubert, I. D. Goepfert, and J. M. Redwing, Appl. Phys. Lett. **71**, 3224 (1997).
- ¹¹A. Billeb, W. Grieshaber, D. Stocker, E. F. Schuber, and R. F. Karlicek, Appl. Phys. Lett. **70**, 2790 (1997).
- ¹²S. J. Xu, G. Li, S. J. Chua, X. C. Wang, and W. Wang, Appl. Phys. Lett. **72**, 2451 (1998).
- ¹³M. Toth, K. Fleischer, and M. R. Phillips, Phys. Rev. B **59**, 1575 (1999).
- ¹⁴M. D. McCluskey, N. M. Johnson, C. G. Van de Walle, D. P. Bour, M. Kneissl, and W. Walukiewicz, Phys. Rev. Lett. **80**, 4008 (1998).
- ¹⁵T. Suski, P. Perlin, C. Skierbiszewski, P. Wisniewski, L. Dmowski, M. Leszczynski, and W. Walukiewicz, Phys. Status Solidi B **216**, 521 (1999).
- ¹⁶J. Neugebauer and C. G. Van de Walle, Appl. Phys. Lett. **69**, 503 (1996).
- ¹⁷C. G. Van de Walle and J. Neugebauer, *III-V Nitrides*, edited by F. A. Ponce, T. D. Moustakas, I. Akasaki, and B. A. Monemar, MRS Symposia Proceedings No. 449 (Materials Research Society, Pittsburgh, 1997), p. 861.
- ¹⁸J. D. Guo, M. S. Feng, and F. M. Pan, Jpn. J. Appl. Phys., Part 1 **34**, 5510 (1995).
- ¹⁹H. R. Kuo, M. S. Feng, J. D. Guo, and M. C. Lee, Jpn. J. Appl. Phys., Part 1 **34**, 44 (1995).
- ²⁰D. K. Gaskill, A. E. Wickenden, K. Doverspike, B. Tadayon, and L. B. Rowland, J. Electron. Mater. **24**, 1525 (1995).
- ²¹P. Hacke, A. Maekawa, N. Koide, K. Hiramatsu, and N. Sawaki, Jpn. J. Appl. Phys., Part 1 **33**, 6443 (1994).
- ²²L. W. Tu, Y. C. Lee, S. J. Chen, I. Lo, D. Stocker, and E. F. Schubert, Appl. Phys. Lett. **73**, 2801 (1998).
- ²³H. Siegle, P. Thurian, L. Eckey, A. Hoffmann, C. Thomsen, B. K. Meyer, H. Amano, I. Akasaki, T. Detchprom, and K. Hiramatsu, Appl. Phys. Lett. **68**, 1265 (1996).
- ²⁴H. M. Chen, Y. F. Chen, M. C. Lee, and M. S. Feng, Phys. Rev. B **56**, 6942 (1997).
- ²⁵G. C. Yi and B. W. Wessels, Appl. Phys. Lett. **69**, 3028 (1996).
- ²⁶K. Saarinen, T. Laine, S. Kuisma, J. Nissila, P. Hautojarvi, L. Dobrzynski, J. M. Baranowski, K. Pakula, R. Stepniewski, M. Wojdak, A. Wyszomolek, T. Suski, M. Leszczynski, I. Grzegory, and S. Porowski, Phys. Rev. Lett. **79**, 3030 (1997).
- ²⁷G. Popovici, W. Kim, A. Botchkarev, H. Tang, H. Morkoc, and J. Solomon, Appl. Phys. Lett. **71**, 3385 (1997).
- ²⁸R. Jones, J. Elsner, M. Haugk, R. Gutierrez, T. Frauenheim, M. I. Heggie, S. Oberg, and P. R. Briddon, Phys. Status Solidi A **171**, 169 (1999).
- ²⁹M. D. Shagalov and A. G. Drizhuk, Opt. Spectrosc. **61**, 646 (1986).
- ³⁰J. T. Hsieh, Ph.D. dissertation, National Tsing Hua University, Taiwan, Republic of China, 2000.