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Characterization of Zn-doped GaN grown by metal–organic vapor phase epitaxy

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Abstract The point defects and photoluminescence (PL) spectra of gallium nitride (GaN) epilayers with Mg, Zn, and unintentional doping were investigated in this study. The concentration of point defects (Ga vacancy and its related complexes) in the Zn-doped GaN is consistent with that in the Mg-doped GaN, but lower than that in undoped GaN. It is suggested that Zn (Mg) atoms occupy Ga sites and suppress the formation of Ga vacancies. Comparing the blue luminescence (BL) band intensity of GaN:Zn with that of GaN:Mg, a factor of 10 strong PL intensity demonstrates that a moderate incorporation of Zn to GaN is likely to improve the structural quality of GaN. Detailed studies on 2.93 eV BL band for GaN:Zn reveal that the Zn related BL band behaves as a donor–acceptor pairs character. For the acceptor level, isolated Zn_{Ga} with the activation energy of 0.386 eV above the valence band is obtained from temperature-dependent PL measurements, whereas the deep donor defect responsible for the 2.93 eV band is deduced to be 164 meV below the conduction band. An O_N–H complex model is suggested to explain the deep donor origin.

Keywords GaN; Metal–organic chemical vapor deposition; Zn-doped; Photoluminescence; Donor–acceptor pairs

1 Introduction

Gallium nitride (GaN) and its ternary and quaternary alloys attracted a great deal of attention for their promising applications in the ultraviolet (UV)-to-blue light emitting diodes (LEDs), laser diodes (LDs), and detecting devices as well as high power and high-temperature electronic devices [1–3]. Recently, Mg-doped GaN, owing to its high-efficient blue emission at about 2.8 eV, is proposed as the potential novel blue fluorescent material for field emission display (FED), which is possible to work at a low acceleration voltage (<50 V) compared with the traditional phosphor [4]. At the same time, Zn-doped GaN, though unsuccessful from the p-type doping point of view, also obtains an increasing interest as novel phosphor [5] because of a much stronger blue emission at 2.85–2.90 eV [6] than that of Mg-doped GaN. To interpret the nature of the higher efficient blue emission in Zn-doped GaN, various models were proposed. Teisseyre et al. [7] suggested that the blue emission in Zn-doped GaN was related to the electron recombination involving a localized donor and Zn acceptor according to the results on hydrostatic pressure and temperature dependence of photoluminescence (PL), and excluded the models of the radiative recombination involving conduct band electron, electron originating from hydrogenic donor states, or of the intra center recombination within a Zn-related defect complex. However, Pankove and Monemar et al. [8, 9] thought that the BL band originated from the transitions, from the conduction band to acceptor level, involving Zn_{Ga} or its related complex.

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Bernardini et al. [10] calculated using the first-principles method and confirmed that Zn_{Ga} was a single acceptor with an ionization energy of 0.33 eV, and a recombination center with emission at 2.95 eV. While the optically detected magnetic resonance (ODMR) investigations showed that the acceptor responsible for the BL band was a Ga-interstitial-related complex [11]. In addition, the reported results on dependence of the BL band on excitation density are controversial. The position of the BL band observed by Monemar et al. [9] remained independent of excitation intensity, however, a marked blue shift was observed with the excitation density increasing in insulating Zn-doped GaN [12]. Therefore, a consensus was not reached on the origination of blue luminescence (BL) in Zn-doped GaN. In this paper, the point defects and optical properties of Zn-doped GaN were investigated using slow-positron annihilation spectroscopy and PL.

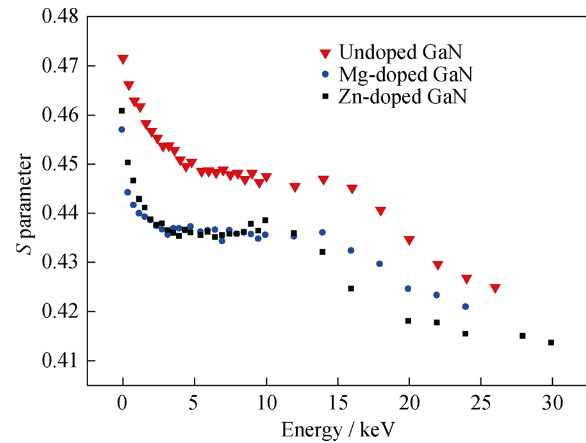

Fig. 1 Low-momentum parameters *S* as a function of incident positron energy in studied GaN layers

2 Experimental

The Zn-doped GaN epilayers were grown on c-plane sapphire substrates using a low-pressure metal–organic vapor phase epitaxy (LP-MOVPE). Prior to growth of the 1 μm thick GaN:Zn layer, a 20 nm thick low-temperature GaN buffer layer was deposited. The growth temperature for the buffer layer was 550 °C, whereas the GaN:Zn layers were grown at 1,030 °C under a pressure of 10,132.5 Pa. Undoped and Mg-doped GaN also were grown for comparison. Trimethylgallium (TMGa), biscyclopentadienylmagnesium (Cp_2Mg), diethylzinc (DEZn), and ammonia (NH_3) were used as sources of Ga, Mg, Zn, and N, respectively. Hydrogen (H_2) was employed as carrier gas. After the growth, the Zn-doped GaN film was divided into four parts which were performed rapid thermal annealing (RTA) at 600, 750, and 900 °C for 10 min in N_2 atmosphere, respectively. Slow-positron annihilation spectroscopy was performed to study the vacancy defects. The positron annihilation experiments were carried out using a beam of monoenergetic positrons from β^+ emission of ^{22}Na. The Doppler broadening of the 511 keV annihilation line was recorded with a Ge detector.

The electrical and optical properties were characterized by room temperature (RT), Hall-effect measurements, and PL. PL was excited with the 325 nm line of a He–Cd laser (30 mW). Weaker excitation densities were achieved using neutral density filters. The PL signal was detected with a cooled GaAs photomultiplier.

3 Results and discussion

Figure 1 shows the low-momentum parameter *S* as a function of the positron beam energy for Zn, Mg, and unintentionally doped GaN, respectively. The *S* parameter for each sample shows a plateau at incident energies $E = 3$–13 keV, where no contribution from the surface to the *S* parameter is detectable. The *S* parameter decreases at higher energies as the positrons reach the substrate and annihilate in the substrate. At $E < 3$ keV, some positrons are able to diffuse onto the sample surface, leading to a high *S* value. Figure 1 shows that the *S* parameter for undoped GaN is larger than that for the Zn- and Mg-doped GaN. Usually, positrons get trapped at neutral and negative vacancies due to the missing positive charge of the ion cores. Positron annihilation in vacancy defects results in an increase of *S* parameter compared with their values in defect-free material because annihilation in defects occurs mainly with low-momentum electron [13]. Therefore, the experimental *S* value indicates that vacancy defects present in the Zn- or Mg-doped GaN are lower than that in the unintentionally doped GaN. The relatively lower *S* parameter obtained for the Zn- or Mg-doped GaN is 0.435 at $E = 3$–13 keV, which is consistent with the value in the reference sample [14]. By investigating the linearity between the annihilation *S* and *W*, all data points for the three samples fall on the same line and the slope of the line is the same as that found in earlier reports [15] for the Ga vacancy in n-type GaN films and bulk crystals. The above results thus suggest that Zn-doped GaN has the same number and the same type of vacancy defects as Mg-doped GaN. Moreover, the observed vacancies are Ga vacancies or its complexes with other atoms.

Figure 2 shows RT PL spectra of samples Zn, Mg, and undoped GaN, respectively. It can be seen that a broad strong 2.93 eV BL for GaN with Zn doping and 2.80 eV BL for GaN with Mg doping dominate the PL spectra. The PL spectrum of undoped GaN exhibits near-band-edge transition at 3.38 eV. Note that the BL band intensity of Zn-doped GaN is about one order of magnitude higher than that of Mg-doped GaN. The studies of Zn codoping with

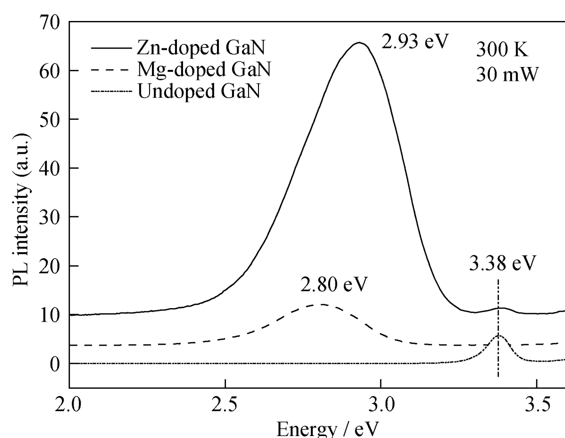

Fig. 2 RT–PL spectra for three samples

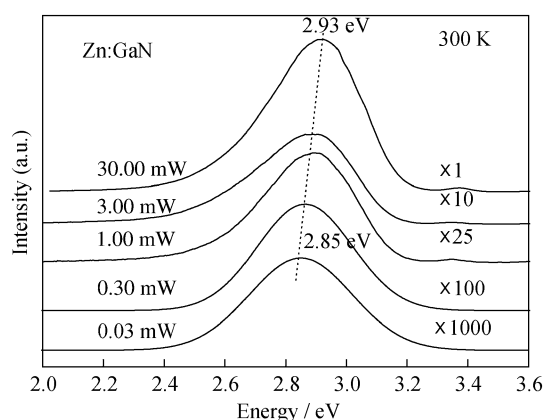

Fig. 3 RT–PL spectra of t Zn-doped GaN at different excitation power densities

Mg find that the incorporation of Zn atoms to Mg-doped GaN produces a low-resistive p-type GaN with a reduction of dislocation density and improvement of the structural qualities of GaN films [12]. Therefore, introduction of a moderate amount of Zn to GaN appears to reduce the defect concentration. Because the number of point defects in the Zn- and Mg-doped GaN is the same, it is suggested that Zn might remove dislocations like the reduction of dislocation by dopants observed in III–V compound semiconductors [16]. Thus, the dislocations-related nonradiative recombination center decreases, leading to high external quantum efficiency, i.e., enhances the PL intensity. In the case of Mg doping, most of points are attributed to the transition between distance donor–acceptor pairs (DAP) according to the dependence of this band on the excitation density [17–19]. In the case of Zn doping, as mentioned above, no consensus is reached on the origin of blue emission. Therefore, in the following section, we will focus on the Zn-doped GaN.

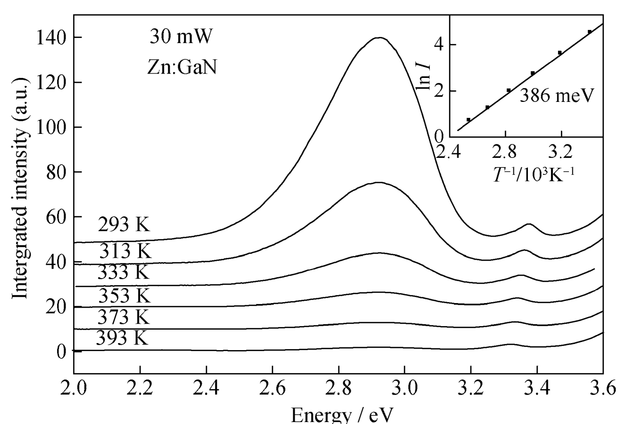

Fig. 4 High-temperature photoluminescence spectra of GaN:Zn. 386 meV thermal activation energy of Zn acceptor being obtained from Arrhenius plot as shown in inset

To clarify the origin of the strong-intensity 2.93 eV BL band, the dependence of the PL emission on excitation density was studied (Fig. 3). From Fig. 3, it is clear that the peak position of the PL emission depends strongly on the excitation density and shifts to higher energy with excitation density increasing. This is probable for DAP recombination involving electrons and holes trapped at distant donors and acceptors, respectively. The equation describes distant DAP recombination as follows [20]:

$$E_{\mathrm{PL}} = E_{\mathrm{g}} - (E_{\mathrm{D}} + E_{\mathrm{A}}) + E_{\mathrm{DAP}} \quad (1)$$

where E_{PL} is the measured peak energy by PL, E_{g} is the bandgap energy of GaN, E_{D} is the donor energy level, and E_{A} is the acceptor energy level; where the symbols have their usual meaning. The last term $E_{\mathrm{DAP}} = \mathrm{e}^2/\varepsilon R$ represents the coulomb attraction energy of an ionized DAP with an intrapair distance R. With the excitation power increasing, besides the DAP separates with longer distance R, those with the shorter distance R will take part in the D–A recombination emission, thus the number of occupied donor and acceptor centers increases and their average distance R necessarily decreases. As a consequence, E_{DAP} increases, and according to Eq. (1), EPL shifts to higher energy. Therefore, it can be concluded that this BL band originates from the DAP transition. Based on PL thermal quenching measurement for 2.93 eV peak, an acceptor level of 386 meV is obtained as shown in the inset of Fig. 4. This value is in good agreement with the calculated ionization energy (367 meV) of Zn acceptor [21]. Setting $E_{\mathrm{DAP}} \approx 0$ in Eq. (1) for the lowest peak position in Fig. 3 and taking $E_{\mathrm{g}} = 3.4$ eV, $E_{\mathrm{A}} = 386$ meV, and then yields $E_{\mathrm{D}} \approx 164$ meV below the conduction band for the donor-related deep level. This value coincides with that (0.15 eV) observed for n-type GaN by deep-level transient spectroscopy [22]. Hence, the 2.93 eV BL band can be assigned as

Table 1 Dopant type and Hall data obtained at RT for studied samples

Samples	Conductive type	Carrier concentration/cm^{-3}
Undoped GaN	n	6×10^{18}
Mg-doped GaN	p	3×10^{17}
Zn-doped GaN		
As-grown	n	4×10^{17}
Annealed	n	6×10^{17}

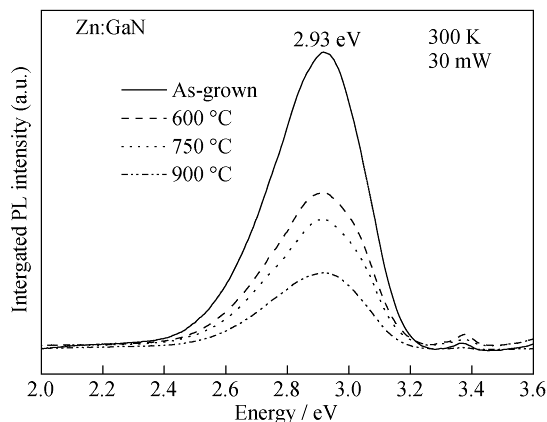

Fig. 5 RT–PL spectra for as-grown and annealed Zn-doped GaN

a DAP recombination involving isolated Zn acceptors and relatively deep donors D.

In the following, we will discuss the origin of the deep donor level. The dopant type and Hall results for the studied samples are listed in Table 1. Considering that the unintentionally doped GaN has a high background electron concentration and Zn-doped GaN is n-type before and after thermal annealing, it is possible that there exits residual oxygen in the reactor. Therefore, the oxygen incorporates into GaN film during growth and substitute oxygen for nitrogen site O_N is the most reasonable, because O_N defect has lower formation energy than that of V_N (nitrogen vacancy) in n-type GaN [23] and ZnO compound is unlikely to form [24]. According to Fig. 5, it demonstrates that the BL peak intensity decreases with thermal annealing temperature increasing for Zn-doped GaN. Koide et al. [25] investigated luminescence properties for the as-grown Mg-doped GaN by low-energy electron-excited nanoluminescence spectroscopy and observed that a rapid reduction of BL intensity with electron exposure times increasing. They explained that the BL was due to the transition between the hydrogen-related deep donor (V_N–H) and the Mg_{Ga} acceptor, and after the electron exposure, the quantities of deep donor decreased because of the dissociation of V_N–H. Therefore, on the one hand, the decrease of BL in this experiment suggests that the deep donor is probably attributed to O_N complex related with hydrogen. During thermal annealing, the following reactions occur for O_N–H complex. Since chemical reaction rate is related with temperature, increasing temperature will speed up the reaction. Hence, with the increase of annealing temperature, the deep donor (O_N–H) concentrations reduce, then the total number of DAP decreases, which is thought to lead to the reduction of BL intensity because the number of DAP has effect on the luminescence intensity. However, further investigations are required to confirm the existence of a local vibrational mode of O–H.

4 Conclusion

The point defects and optical properties of the unintentionally, Mg- and Zn-doped GaN epilayers were investigated using slow-positron annihilation spectroscopy and PL measurements. The number of point defects in the Zn-doped GaN is consistent with that in the Mg-doped GaN, but lower than that in the undoped GaN. Comparing the BL emission intensity of GaN:Zn with that of GaN:Mg, a factor of 10 strong PL intensity demonstrates that a moderate incorporation of Zn to GaN can improve the structural quality of GaN. Detailed studies on 2.93 eV BL band in GaN:Zn show that the Zn-related BL band has a D-A pair recombination character involving a deep donor and shallow acceptor, where Zn_{Ga} is the reasonable model to explain the generation of the shallow acceptor level. O_N–H complex model is tentatively used for explaining the origin of deep donor level.

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References

[1] Song YM, Choi ES, Park GC, Park CY, Jang SJ, Lee YT. Disordered antireflective nanostructures on GaN-based light-emitting diodes using Ag nanoparticles for improved light extraction efficiency. Appl Phys Lett. 2010;97(9):093110.

[2] Li DB, Hu WG, Miyake H, Hiramatsu K, Hiramatsu K, Song H. Enhanced deep ultraviolet emission from Si-doped $Al_xGa_{1-x}N$/AlN MQWs. Chin Phys B. 2010;19(12):127801.

[3] Li DB, Sun XJ, Song H, Li ZM, Chen YR, Jiang H, Miao GQ. Realization of a high-performance GaN UV detector by nanoplasmonic enhancement. Adv Mater. 2012;24(6):845.

[4] Li DB, Nakamura K, Miyake H, Hiramatsu K, Kobayashi M, Kikuta S. Enhancement of blue emission from Mg-doped GaN activated at low temperature in O_2/N_2 mixture. Phys Status Solidi C. 2006;3(8):2750.

[5] Kanie H, Kawano T, Sugimoto K, Kawai R. Nitride phosphors for low voltage cathodoluminescence devices. Mater Res Soc Symp Proc. 2000;621:Q5.11.1.

[6] Pankove JI. Luminescence in GaN. J. Photoluminescence in doped GaN bulk crystal. Luminescence. 1973;7(3–4):114.

[7] Teisseyre H, Perlin P, Suski T, Grzegory I, Jun J, Porowski S. Photoluminescence in doped GaN bulk crystal. J Phys Chem Solids. 1995;56(3–4):353.
[8] Pankove JI, Berkeyheiser JE, Miller EA. Properties of Zn-doped GaN I. Photoluminescence. J Appl Phys. 1974;45(3):1280.
[9] Monemar B, Lagerstedt O, Gislason HP. Properties of Zn-d oped VPE-grown GaN. I. Luminescence data in relation to doping conditions. J Appl Phys. 1980;51(1):625.
[10] Bernardini F, Fiorentini V, Nieminen R. Zn-Related Deep Centers in wurtzite GaN. In: Scheffler M, Zimmerman R, editors. Singapore: World Scientific; 1996;2881.
[11] Hai PN, Chen WM, Buyanova IA, Monemar B, Amano H, Akasaki I. Ga-related defect in as-grown Zn-doped GaN: an optically detected magnetic resonance study. Phys Rev B. 2000;62(16):10607.
[12] Kim KS, Han MS, Yang GM, Youn CJ, Lee HJ, Cho HK, Lee JY. Codoping characteristics of Zn with Mg in GaN. Appl Phys Lett. 2000;77(8):1123.
[13] Saarinen K, Hautojarvi P, Corbet C. Identification of Defect in Semiconductors. In: Stavola M, editor. New York: Academic; 1998;210.
[14] Saarinen K, Seppala P, Oila J, Hautojärvi P, Corbel C, Briot O, Aulombard RL. Gallium vacancies and the growth stoichiometry of GaN studied by positron annihilation spectroscopy. Appl Phys Lett. 1998;73(22):3253.
[15] Saarinen K, Laine T, Kuisma S, Nissilä J, Hautojärvi P, Dobrzynski L, Baranowski JM, Pakula K, Stepniewski R, Wojdak M, Wysmolek A, Suski T, Leszczynski M, Grzegory I, Porowski S. Observation of native Ga vacancies in GaN by positron annihilation. Phys Rev Lett. 1997;79(16):3030.
[16] Ohbu I, Ishino M, Mozume T. Effects of indium doping on crystalline qualities of GaAs on Si by molecular beam epitaxy. Appl Phys Lett. 1989;54(4):396.
[17] Kafmann U, Kunzer M, Maier M, Obloh H, Ramakrishnan A, Santic B, Schlotter P. Nature of the 2.8 eV photoluminescence band in Mg doped GaN. Appl Phys Lett. 1998;72(11):1326.
[18] Reshchikov MA, Yi GC, Wessels BW. Behavior of 2.8- and 3.2-eV photoluminescence bands in Mg-doped GaN at different temperatures and excitation densities. Phys Rev B. 1999;59(20):13176.
[19] Qu BZ, Zhu QS, Sun XH, Wan SK, Wang ZG, Nagai H, Kawaguchi Y, Hiramatsu K, Sawaki N. Photoluminescence of Mg-doped GaN grown by metalorganic chemical vapor deposition. J Vac Sci Technol A. 2003;21(4):838.
[20] Williams FE. Donor–acceptor pairs in semiconductors. Phys Status Solidi. 1968;25(2):493.
[21] Wang H, Chen AB. Calculations of acceptor ionization energies in GaN. Phys Rev B. 2001;63(12):125212.
[22] Götz W, Johnson NM, Bour DP, Chen C, Liu H, Kuo C, Imler W. Shallow and deep level defects in GaN. Mater Res Soc Symp Proc. 1996;395(75):9571.
[23] Mattila T, Nieminen RM. Point-defect complexes and broadband luminescence in GaN and AlN. Phys Rev B. 1997;55(15):9571.
[24] Jablonska KL, Suski T, Gorczyca I, Christensen NE, Liberal J, Kachniarzl J, Lagarde P, Cortes R, Grzegory I. Anisotropy of atomic bonds formed by p-type dopants in bulk GaN crystals. Appl Phys A. 2002;75(5):577.
[25] Koide Y, Walker DE Jr, White BD, Brillson LJ, Murakami M, Kamiyama S, Amano H, Akasaki I. Simultaneous observation of luminescence and dissociation processes of Mg–H complex for Mg-doped GaN. J Appl Phys. 2002;92(7):3657.