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Rapid thermal annealing effects on blue luminescence of As-implanted GaN

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Rapid thermal annealing effects on blue luminescence of As-implanted GaN grown by metalorganic vapor phases epitaxy were investigated by means of photoluminescence and photoluminescence excitation measurements. The locations of the As-implantation induced bands and the associated transition channels for the emission were determined to characterize the As-implanted GaN. After the rapid thermal annealing treatment, the deep As-related levels become more ready to be populated by photoexcitation at low temperature so that the new blue luminescence emission peak is enhanced significantly, whose activation energy is found to be 46 meV. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1503160]

Over the past few years, much research has been focused on the doping of group III-nitrides because of their optoelectronic applications.[1,2] In particular, the isoelectronic doping effect has also been explored to improve significantly the electrical and optical properties of GaN.[3,4] As doping is such a case in which large band-gap bowing, strong blue emission and cubic structure are intriguing for investigation.[5] However, since the first observation of blue emission from As-implanted GaN was reported in 1976,[6] there were not many articles addressing the mechanism responsible for this emission due to difficulties in sample preparation. Thus, the details concerning radiative transition channels are not fully understood yet, though they are attributed to some sort of defects such as dislocations and vacancies. In this article, we made close examination of the rapid thermal annealing (RTA) effects on the blue emission of As-implanted GaN through photoluminescence (PL) and photoluminescence excitation (PLE) measurements, following our previous works on isoelectronic (In and As) doped GaN.[7,8] Possible defect levels are proposed and the activation energy for the blue emission is deduced.

The undoped GaN films were grown on the (0001) sapphire substrate at 1050 °C by using metalorganic vapor phase epitaxy (MOVPE). The As-implantation doses were prepared between 10^{17} and 10^{21} cm^{-3}. These samples were treated with RTA at a temperature 1100 °C for different duration (10, 20 and 30 s) under flowing N_2 gas and using the proximity cap method to repair the implantation damages. In PL, a He–Cd laser (Kimmon IK 5552R-F) operating at 325 nm was used for above band-gap excitation, combined with a monochromator (ARC-500) and a photomultiplier tube (Hamamatsu R-955) for detection. Various sample temperatures were achieved between 18 and 300 K in a closed-cycle refrigeration (APD Cryogenics HC-2). For PLE measurements, an 150 W xenon arc lamp combined with a monochromator (PTI 101) was employed as the excitation light source. The detection system is the same as that used in PL works. All the PLE spectra have been corrected by the Xe light source response throughout the measured spectral range.

As shown in Fig. 1, typical PL spectra of As-implanted GaN reveal a weak I_2 line at 357 nm (donor bound exciton, D^0X) as compared with the enhanced yellow luminescence (YL). It is due to the increased defects from implantation induced damages which are undesirable and need remedy. Since the RTA is commonly employed to improve sample quality, we have applied RTA on our samples at 1100 °C for 10, 20 and 30 s and observed drastic change in the PL intensity after annealing, and the I_2 to YL intensity ratio rises rapidly. In addition, the blue luminescence (BL) appears stronger and more prominent with an increasing annealing time. Obviously, the film quality was improved progressively by RTA, although it generated additional localized states responsible for the BL. According to Van De Walle *et al.*,[9] these localized states are likely due to substitutional As_{Ga} sites that can form deep double donors because of similar atomic size and reasonable formation energy.

Although there are already many discussions about the YL mechanism, the PLE studies should provide further convincing data for its interpretation. In this work, we have applied PLE technique to monitor the YL peak (~560 nm) from unannealed GaN:As of different doses. Similar to the results of P-implanted GaN,[8] the PLE spectra at 300 K also revealed a sharp peak at 366 nm with a width of ~5 nm which is about 28 meV below the I_2 line in Fig. 2(a). This new impurity band just below the shallow donor level (D^0X) is formed by As implantation. It offers a relaxation channel that is more efficient for the YL than the usual band-to-band transitions in as-grown sample. Thus the YL involves the

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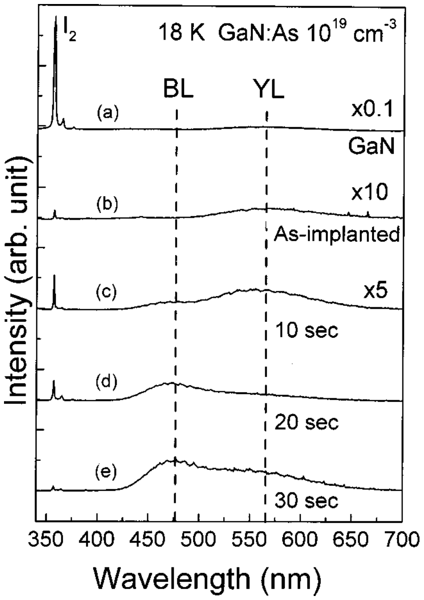

FIG. 1. 18 K PL spectrum of (a) as-grown GaN, (b) As-implanted GaN (10^{19} cm^{-3}), (c) after 10 s RTA, (d) after 20 s RTA and (e) after 30 s RTA.

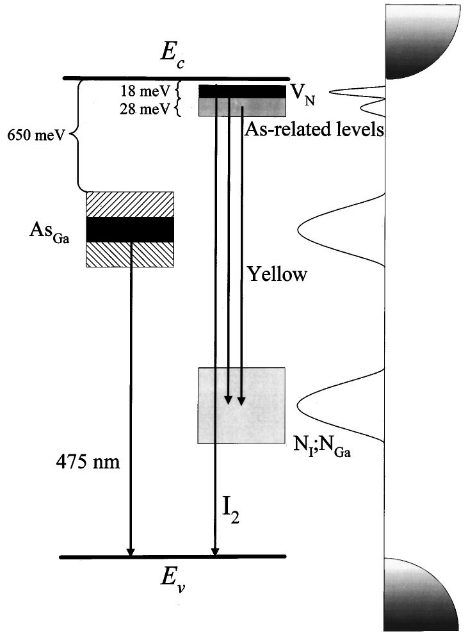

FIG. 3. Schematic energy diagram of As-implanted GaN is proposed to account for the corresponding transitions with possibility distribution on the right.

radiative recombination between shallow levels and deep localized states. From two first-principle total energy calculations, the N_I is such a deep acceptor at ~1 eV above the valence band maximum.[10,11] The neutral N_{Ga} is also such a deep-hole trap according to Jenkins *et al.* and Mattila *et al.*[12,13] Our results appear to be consistent with the model proposed by Ogino and Aoki and also by Hofmann *et al.*[14,15] Obviously, ion-implantation incurred defects are associated with both shallow and deep double donors (i.e., As_{Ga}) and competition should be present among them for capturing photoexcited electrons that resulted in variations of BL and I_2 intensities as can be seen in Figs. 1(c)–1(e).

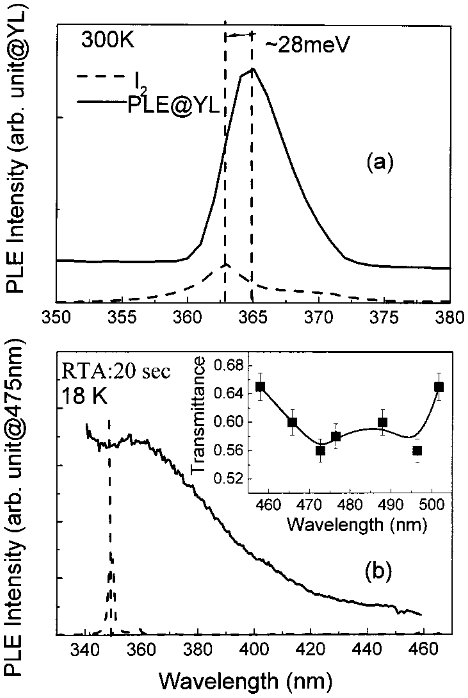

FIG. 2. (a) Room temperature PLE spectrum for the YL of the unannealed GaN:As (10^{19} cm^{-3}) detected at 560 nm (YL). The PLE peak is 28 meV below the I_2 emission level. (b) 18 K PLE spectrum for the BL of GaN:As reveals a rising step towards the I_2 line. The inset shows the real absorption spectra in the blue range as due to As-incorporation after RTA.

Regarding the BL, we also applied the PLE spectroscopy monitoring the 475 nm emission to see whether there is any clear absorption peak about the band gap energy. In contrast to our expectations, PLE signals show a gradual increase toward the I_2 line and stay relatively unchanged above the band gap [see Fig. 2(b)]. It is believed that, shortly after photo-excitation of both native shallow donor levels and the conduction band, deep donors are subsequently populated for the final BL transitions to the valence band. To ensure the existence of these deep donors, we carried out the absorption measurements across the BL peak by using different wavelengths of Ar^+ laser, which is covered from 457.9 to 514.5 nm. The transmittance shows a dip ~480 nm [see the inset of Fig. 2(b)], reflecting that the incorporation of As into GaN forms a new deep level band, likely As_{Ga} donors.

Based on the available data, we proceed to propose a schematic energy diagram in Fig. 3. The familiar shallow level (native defect V_N) responsible for the I_2 line is located at 18 meV below the conduction band.[8] The other level located at ~28 meV further below the I_2 line is introduced by As implantation that contributes to the YL. Furthermore, because of ion implantation, the new broad band (extra deep levels) is also formed at 2.65 eV above the valence band which gives rise to the BL about 475 nm.[14]

In order to obtain the activation energy for the As-related deep levels (likely As_{Ga}) in GaN, we measured the temperature dependent PL spectra between 18 and 300 K in Fig. 4. Dramatic changes in the BL intensity were observed across the above temperature range. Using the following formula:

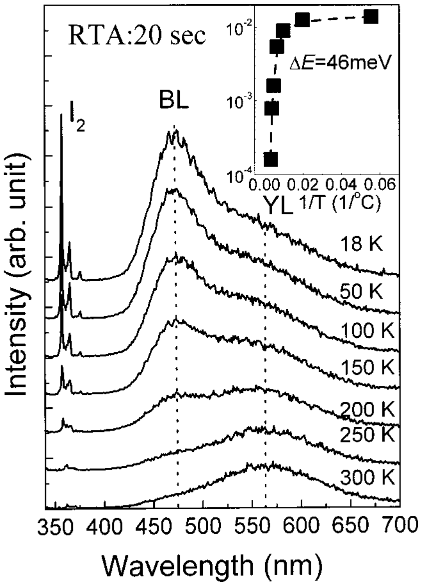

FIG. 4. PL spectrum of 10^{19} cm^{-3} As-implanted GaN between 18 and 300 K. The Arrhenius plot in the inset indicates an activation energy of 46 meV.

$$I(0)/I(T)=[1+C\ \exp(-\Delta E/kT)],$$

where ΔE is the activation energy and C is a constant,[16] we are able to fit the experimental data in a logarithmic scale that is shown in an Arrhenius plot of Fig. 4. From the slope, the activation energy ΔE is calculated to be 46 meV, which is close to 50 meV reported by Li *et al.*[17] At temperatures higher than 150 K, these As-related states are easily depopulated so that the BL diminishes rapidly. The I_2 line weakening is also evident because of its small activation energy. In contrast then, the YL becomes the only dominant profile at high temperatures reflecting that native defects are still present regardless of the annealing process. Therefore, our studies reveal that the RTA process not only recovers many defects induced by As-implantation but also enhances the $\mathrm{As_{Ga}}$ substitution. In addition, it also makes better surface and interface flatness.

In summary, we examined As-implanted GaN by using the PL and PLE spectroscopy. The results reflect that the As-implantation introduced various defect levels that also contribute to the YL as a dominant feature in PL spectra before the RTA process. However, after the RTA treatment, the deep As-related levels become more ready to be populated by photo-excitation at low temperature so that the new BL emission peak is enhanced significantly, whose activation energy is found to be 46 meV. The absorption measurements provide further evidence for the existence of these deep levels, which might be attributed to the $\mathrm{As_{Ga}}$ substitution effect.

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[1] H. Amano, M. Kito, K. Hiramatsu, and I. Akasaki, Jpn. J. Appl. Phys., Part 2 **28**, L2112 (1989).
[2] S. Nakamura, N. Iwasa, M. Senoh, and T. Mukai, Jpn. J. Appl. Phys., Part 1 **31**, 1258 (1992).
[3] C. K. Shu, J. Ou, H. C. Lin, W. K. Chen, and M. C. Lee, Appl. Phys. Lett. **73**, 641 (1998).
[4] H. M. Chung, W. C. Chuang, Y. C. Pan, C. C. Tsai, M. C. Lee, W. H. Chen, W. K. Chen, C. I. Chiang, C. H. Lin, and H. Chang, Appl. Phys. Lett. **76**, 897 (2000).
[5] S. H. Wei and A. Zunger, Phys. Rev. Lett. **76**, 664 (1996).
[6] J. I. Pankove and J. A. Hutchby, J. Appl. Phys. **47**, 5387 (1976).
[7] H. Y. Huang, W. C. Lin, W. H. Lee, C. K. Shu, K. C. Liao, W. K. Chen, M. C. Lee, W. H. Chen, and Y. Y. Lee, Appl. Phys. Lett. **77**, 2819 (2000).
[8] H. Y. Huang, C. H. Chuang, C. K. Shu, Y. C. Pan, W. H. Lee, W. K. Chen, W. K. Chen, and M. C. Lee, Appl. Phys. Lett. **80**, 3349 (2002).
[9] C. G. Van de Walle and J. Neugebauer, Appl. Phys. Lett. **76**, 1009 (2000).
[10] M. Kuball and J. M. Hayes, J. Appl. Phys. **87**, 2736 (2000).
[11] T. Mattila and A. Zunger, Phys. Rev. B **58**, 1367 (1998).
[12] D. W. Jenkins and J. D. Dow, Phys. Rev. B **50**, 8067 (1989).
[13] T. Mattila and A. Zunger, Phys. Rev. B **59**, 9943 (1999).
[14] T. Ogino and M. Aoki, Jpn. J. Appl. Phys., Part 1 **18**, 1049 (1979).
[15] A. Hofman, L. Eckey, P. Maxim, J. Cr. Holst, R. Heitz, D. M. Hofmann, D. Kovalev, G. Steude, D. Volm, B. K. Meyer, T. Detchprohm, H. Amano, and I. Akasaki, Solid-State Electron. **41**, 275 (1997).
[16] J. Li, K. B. Nam, J. Y. Lin, and H. X. Jiang, Appl. Phys. Lett. **79**, 3245 (2001).
[17] X. Li, S. Kim, E. E. Reuter, S. G. Bishop, and J. J. Coleman, Appl. Phys. Lett. **72**, 1990 (1998).