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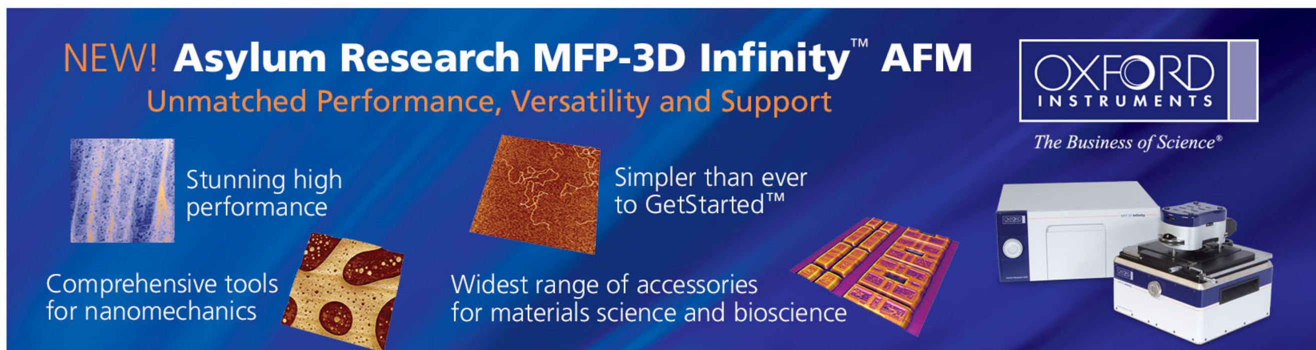


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# Photoluminescence and photoluminescence excitation studies of as-grown and P-implanted GaN: On the nature of yellow luminescence

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We have studied optical and electronic properties of isoelectronic P-implanted GaN films grown by metalorganic chemical vapor phase epitaxy. After rapid thermal annealing, a strong emission band around 430 nm was observed, which is attributed to the recombination of exciton bound to isoelectronic P-hole traps. From the Arrhenius plot, the hole binding energy of ~180 meV and the exciton localization energy of 28 meV were obtained. According to first-principle total-energy calculations, the implantation process likely introduced $N_I$ and P-related defects. By using photoluminescence excitation technique, we found that the P-implantation-induced localized states not only increase the yellow luminescence but also suppress the transitions from the free carriers to deep levels. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1476400]

Although the group-III nitride materials have been fabricated for ultraviolet-to-green light-emitting diodes, laser diodes, vertical cavity surface emitting lasers and heterojunction bipolar transistors,[1–3] they are still having a high defect density problem due to large lattice mismatch. Isoelectronic doping has demonstrated improved crystalline quality as well as the electrical and optical properties in typical III–V and II–VI semiconductors, for instance, N-doped GaP (Ref. 4) and In-doped GaAs.[5,6] Previously, we studied the isoelectronic In-doped GaN grown by metalorganic chemical vapor phase epitaxy, and found that the small mount of In atom incorporation indeed brought improvements on the optical, electronic, and crystal qualities.[7–9] In this work, we extended to the group-V elements using the isoelectronic P implantation into GaN and investigated its effects on optical and electrical properties.

The undoped GaN films were grown on the (0001) sapphire substrate at 1050 °C by MOVPE. The P-implanted GaN (GaN:P) films were prepared with different doses between $10^{14}$ and $10^{16}$ cm$^{-2}$. The samples were later treated with rapid thermal annealing (RTA) at a temperature 1100 °C for different durations (10, 20, and 30 s) under flowing $N_2$ gas using proximity cap method to recover implantation damages. For the photoluminescence (PL) measurements, we utilized a He–Cd laser (Kimmon IK 5552R-F) operating at 325 nm for above-band-gap excitation, and a 0.5 m monochromator and a photomultiplier tube (Hamamatsu R-955) for detection. The samples were held in a closed-cycle refrigerator (APD Cryogenics HC-2) for temperature varying measurements between 18 and 300 K. For photoluminescence excitation (PLE) measurements, we used a 150 W Xenon arc lamp combined with a scanning monochromator (PTI 101) as an excitation light source. The luminescence signals were detected by the same PL system. The PLE spectra were all corrected by the Xe light source response.

Despite of impressive progresses made in the GaN-based devices, there are numbers of defects in this wide band gap material remained to be studied.[10–12] Some of them are responsible for forming deep levels that give rise to the notorious "yellow luminescence" (YL) (Fig. 1). In addition to the YL intensified in increasing temperatures, the prominent $I_2$ line at 357 nm (donor bound exciton, $D^0X$) is the only dominant peak at low temperature. This reveals that not only that the bound exciton is ionized but deep levels are also activated significantly at a high temperature. Researchers often infer the film quality by the intensity ratio of YL to $I_2$.

Conventionally, there are two major models interpreting the YL transition. One proposed by Glaser argued that the YL is from the deep double-donor to shallow (effective-mass) acceptor transition.[13] The other one proposed by Ogino and Aoki,[14] and also by Hofmann *et al.*,[15] attributed the YL to the radiative recombination between shallow-donor to deep localized acceptor levels. According to Jenkins *et al.*[16] the neutral antisite, $N_{Ga}$, is such a deep-hole trap.

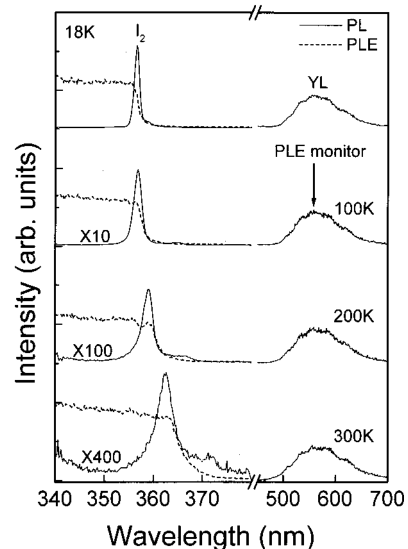


FIG. 1. The temperature dependent PL of as-grown GaN and PLE spectra monitored at YL.

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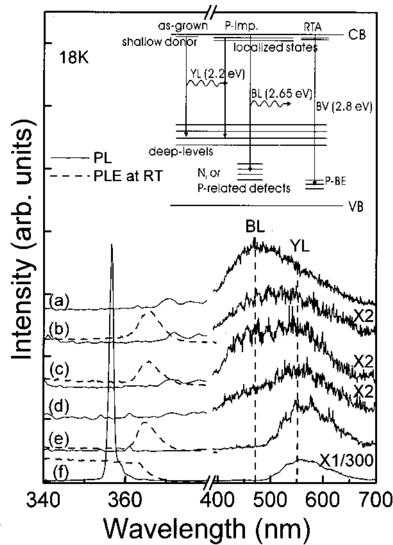


FIG. 2. The 18 K PL spectra of GaN:P under different P-implantation doses. (a) $10^{16}$ cm$^{-2}$, (b) $5\times10^{15}$ cm$^{-2}$, (c) $10^{15}$ cm$^{-2}$, (d) $5\times10^{14}$ cm$^{-2}$, (e) $10^{14}$ cm$^{-2}$, and (f) unimplanted. The dashed curves show the room temperature PLE spectra.

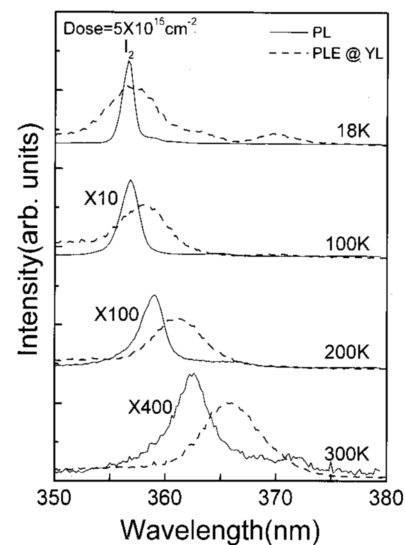


FIG. 3. The temperature dependent PLE spectra of P-implanted ($5\times10^{15}$ cm$^{-2}$) GaN after 30 s RTA compared with the $I_2$ line of as-grown GaN.

Mattila *et al.* argued that since a strong electron–phonon interaction is associated with the large atomic displacement of $N_{\mathrm{Ga}}$, it is likely to be a favor candidate for the YL.[17] Our measured Raman $A_1$ (LO) mode showed significant broadening, the electron–phonon coupling might also involved in the wide YL transition.

To investigate the transition channels for the YL, we have probed its peak signals at 550 nm with the PLE spectroscopy and observed a clear absorption step about the band gap energy (see the broken line in Fig. 1). Since this step overlaps with the $I_2$ line, it shows the broadness of absorption edge contributing to the YL intensity. As the temperature is raised above 100 K, some levels slightly lower than that for the $I_2$ line may also help the YL transition. It is reasonable to infer that nearly all of the native shallow-donor levels are occupied at low temperature so that transitions to them from the valence band are effectively prohibited. At higher temperatures, a significant fraction of the donors is ionized to allow increased photoexcitation to these levels. Therefore, the PLE studies of as-grown GaN have revealed the connection between the native shallow donors and the YL.

We next address whether the YL profile is affected by ion implantation. We found that the Raman $E_2$ mode has an insignificant shift but broadens only slightly so that the crystalline structure of GaN:P should remain essentially unchanged. However, drastic changes in the PL spectra were observed in Fig. 2. First, the prominent $I_2$ line is quenched. Second, a new broad band appears around 467 nm (2.65 eV). This blue luminescence (BL) becomes dominant at the highest dose along with the residual YL. Thus, it is obvious that the implantation process produced extra deep levels that are responsible for the BL. According to two first-principle total energy calculations the nitrogen interstitial defect, $N_I$, is a single deep acceptor at approximately 1 eV above the valence band maximum.[18,19] *Ab initio* calculations showed that the native nitrogen vacancy defect, $V_N$, is a shallow donor in high concentration. We tend to ascribe the BL to the radiative recombination between $V_N$ and $N_I$ (and/or other P-related defect levels) caused by P-implantation (refer to the schematic diagram in the inset of Fig. 2).

As far as the PLE spectra probed at the YL for GaN:P are concerned, we have detected a rather intense and also broad peak next to the $I_2$ line, instead of the step profile observed in the as-grown GaN (see the dashed curves in Fig. 2). Obviously, the P implantation also generated additional localized states just below the native shallow-donor level that can greatly enhance the YL through below band gap absorption. It is noticed that these localized states have uneven distribution toward the low energy side with the increasing dose, reflecting implantation-induced defect levels are deeper than that of the shallow donor. Besides, they appear to be more efficient than the shallow donors in relaxing excess carriers in the conduction band to quench the $I_2$ line. Pankove *et al.* used different ions for implantation into GaN and also observed such an enhancement effect in YL.[20] Guénaud *et al.* studied Fe-implanted GaN and suggested that band-to-band absorption can contribute to both the $I_2$ and YL emissions while bound exciton absorption preferentially enhance the YL than the $I_2$.[21] Our PLE results for GaN:P seemed to agree with these views and therefore, allowed us to attribute these localized states to the disorder induced by the implantation process. They would not be discoverd if the PLE technique had not been utilized.

Since the defect levels associated with the YL are undesirable, they need to be reduced as much as possible. The RTA is a commonly employed as a remedy to improve sample quality. After the RTA treatment at 1100 °C for 10, 20, and 30 s for different dosages, we measured the PLE profile again. The results become more symmetric without peak position shift as if the levels on the low energy side are renormalized. However, this profile is still broader than the $I_2$ line and peaked at $\sim$2 nm toward the red side independent of annealing duration. Only by varying the sample temperature, the PLE peak is found to shift with respect to the $I_2$ line of as-grown GaN (see Fig. 3). Obviously, a new impurity

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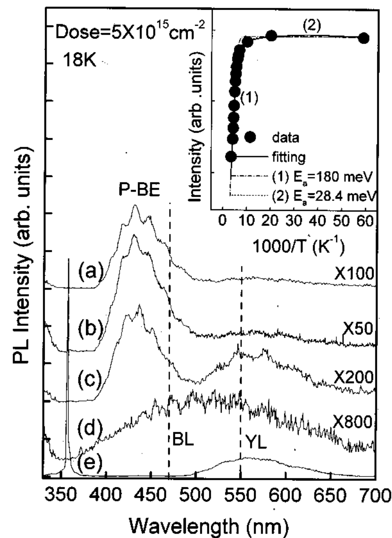


FIG. 4. The 18 K PL spectra of P-implanted GaN after RTA. (a) 30 s, (b) 20 s, (c) 10 s, (d) as-implanted, and (e) as-grown.

band (from localized states) near the shallow-donor level must have formed in GaN:P that provides a more efficient relaxation channel for the YL than the usual band-to-band transitions in as-grown sample.

Dramatic changes in the low temperature PL spectra were also observed after annealing. As shown in Fig. 4, the $I_2$ line is still absent, but a large blue-violet (BV) emission band having a width more than 60 nm appears at 430 nm (2.88 eV). This BV band is likely to be the shifted BL band of the unannealed GaN:P. One report had attributed it to the recombination of excitons bound to isoelectronic-P trap (P-BE) at the N site ($P_N$). Because the electronegativity of P (2.19) is smaller than that of N (3.04) ($\sim$28%),[22] the isoelectronic-P potential becomes more attractive to a hole. Besides, the large lattice distortion due to larger P-atomic size induces hole-like traps and forms holes. These traps can capture free electrons creating bound excitons or interact with electrons at donor site to make D-to-P trap transitions. By increasing the annealing duration, the intensity ratio of P-BE to YL also increases while the P-BE line width decreases. Thus, the $P_N$ substitution is increased that apparently suppresses the relaxation transition from the shallow donor to the deep levels. Because of the microcavity effect, quite a few oscillations on top of this new emission band are also observed.[23] They reveal that the annealing process not only recovers $N_I$ defects formed by P implantation but also makes better surface perfection and interface flatness.

By drawing the temperature dependent intensity of P-BE in an Arrhenius plot (see the inset of Fig. 4), we obtained two activation energies: the hole binding energy ($E_{a1}$) at the isoelectronic-P trap and the exciton localization energy ($E_{a2}$).[24] $E_{a1}$ is 180 (168) meV that is much larger than $E_{a2}$ of 28 (17) meV after 30 (20) s of RTA. Because the $I_2$ localization energy (5.3 meV)[25] is much smaller than that of P-trap, the excited free excitons tend to be trapped. Therefore, it is clear that RTA process makes the $P_N$ substitution more consolidated. Additionally, Hall measurements showed that the reduced mobility ($\sim$2 cm/V s) and increased concentration ($\sim 2.9\times 10^{17}$ cm$^{-3}$) due to implantation can be recovered ($\sim$142 cm/V s, $\sim 6\times 10^{16}$ cm$^{-3}$) just after 10 s of RTA. This also supports improved $P_N$ substitution that apparently suppresses the relaxation transition from the free carriers to the deep levels.

In summary, we have examined the P-implanted GaN by using the PL and PLE spectroscopies. The results revealed that the YL is not only associated with deep levels, but also closely related to the implantation-induced defects that showed a localized distribution. The new PL emission peak is attributed to the P-BE that showed two activation energies.

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