

Photoluminescence of erbium-implanted GaN and *in situ*-doped GaN:Er

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The photoluminescence of *in situ*-doped GaN:Er during hydride vapor phase epitaxy was compared to an Er-implanted GaN sample. At 11 K, the main emission wavelength of the *in situ*-doped sample is shifted to shorter wavelengths by 2.5 nm and the lifetime is 2.1 ± 0.1 ms as compared to 2.9 ± 0.1 ms obtained for the implanted sample. The 295 K band edge luminescence of the *in situ*-doped sample was free of the broad band luminescence centered at 500 nm which dominated the spectrum of the implanted sample. Reversible changes in the emission intensity of the *in situ*-doped sample upon annealing in a N₂ versus a NH₃/H₂ ambient indicate the probable role of hydrogen in determining the luminescence efficiency of these samples. © 1998 American Institute of Physics. [S0003-6951(98)02010-5]

The rare-earth element erbium in the trivalent state (Er³⁺) has received considerable attention since the $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition at 1540 nm coincides with a minimum in loss in silica optical fibers.¹ This transition occurs between energy levels within the shielded 4f electron shell, making the optical transitions of Er³⁺ sharp, as well as relatively insensitive to temperature and host affects.² These luminescence properties make erbium-doped semiconductors an appealing material system for application in optoelectronic devices.

One problem which plagues the development of a practical erbium-doped semiconductor device is the pronounced temperature quenching of the rare-earth luminescence within most semiconductor hosts. Favennec *et al.* discovered that quenching of the rare-earth luminescence was reduced in wide band-gap semiconductor hosts.³ This discovery has led to several investigations of Er-implanted GaN.^{4–12} GaN is a wide band-gap III–V semiconductor useful as a short wavelength emitter and detector.¹³ Previous investigations of Er luminescence in GaN:Er have been promising with most researchers finding only an ~50% decrease in photoluminescence intensity over the temperature range 6–300 K.^{4,8,9,11} This is a significant improvement over the two-to-three order of magnitude decrease of Er luminescence intensity in GaAs:Er.²

The studies performed on GaN:Er so far have principally focused on Er implanted into GaN. The large mass of the Er implant species limits this technique to the formation of thin layers of GaN:Er with a high amount of residual implant-related damage. In this letter, we report a photoluminescence study of *in situ*-doped GaN:Er during hydride vapor phase epitaxy (HVPE) using elemental Er as the *in situ* dopant and Er implanted into nominally undoped GaN also grown by HVPE. HVPE is an established technique for GaN growth and is capable of providing high growth rates and thick GaN layers.^{13,14} The *in situ* doping of GaN with Er during HVPE growth should result, therefore, in thick, uniformly doped layers. Low temperature Er³⁺ luminescence of the *in situ*-doped sample is observed with the peak intensity at 1536.5

nm and an 11 K lifetime of 2.1 ± 0.1 ms. The Er³⁺ luminescence was no longer detectable above 150 K so the temperature quenching to room temperature could not be determined. The band edge luminescence spectra showed considerable structure between 380 and 390 nm at 11 K evolving into a broad band centered at 390 nm at 295 K.

In situ-doped GaN:Er was grown in a horizontal HVPE reactor. The nitrogen precursor was NH₃. A Ga:Er solution held in a quartz boat at 880 °C served as both the group III and dopant source. According to the phase diagram, the binary Ga–Er system forms a miscible liquid from 0 to 27 wt % Er at $T=880$ °C. The transport of Er to the growing GaN crystal structure occurred most probably via ErCl₃. This assumption was based on theoretical work which showed that the stability of other gas phase rare-earth chlorides followed the trend RECl₃ > RECl₂ > RECl.¹⁵ Although data regarding the vapor pressure of this species were scarce, one source did indicate that ErCl₃ has a pressure of 2 Torr at $T=950$ °C.¹⁶ The Ga:Er boat was kept at a lower temperature, but this datum indicates that ErCl₃ probably had a significant vapor pressure even at 880 °C. A GaN:Er layer, 20 μm thick, was grown at a V/III ratio of 30 and a substrate temperature of 1030 °C. SIMS was performed on the *in situ*-doped sample and revealed a peak Er concentration of 2×10^{19} atoms/cm⁻³ at 0.1 μm falling to a steady concentration of 1×10^{18} atoms/cm⁻³ through the remainder of the layer.

The implantation samples were nominally undoped GaN grown on (0001) sapphire by HVPE as previously reported.¹⁴ Prior to ion implantation the band edge luminescence spectra at 11 K showed a dominant structure at 357.2 nm (3.472 eV). Er was implanted into GaN at 300 keV with a dose of 2×10^{14} atoms/cm². Secondary ion mass spectrometry (SIMS) data indicate that the peak Er concentration was 5.3×10^{19} atoms/cm³ at a depth of 33.1 nm. Oxygen was coimplanted into the GaN at 40 keV and a dose of 2×10^{15} atoms/cm². SIMS was not used to determine the O concentration, but calculations estimate a peak concentration of 3.4×10^{20} atoms/cm³ at a depth of 54.0 nm. As reported previously, oxygen enhances or activates the Er luminescence in the GaN host.^{4–6,8–11} The samples showed no band

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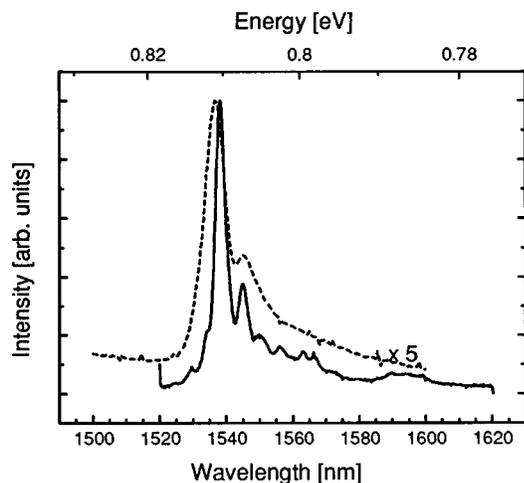


FIG. 1. 11 K photoluminescence spectra of the Er^{3+} emission obtained with 488 nm excitation. The dashed line is from *in situ*-doped GaN:Er grown by HVPE. The solid line is for Er and O coimplanted into GaN grown by HVPE.

edge or Er related luminescence prior to annealing. The annealing conditions were 800 °C for 0.5 h in a flowing NH_3/H_2 ambient.⁹

Er^{3+} luminescence was excited with an average power of 100 mW from the 488 nm line of an Ar ion laser. The sample temperature was controlled between 11 and 295 K with a variable temperature cryostat. The Er^{3+} luminescence was dispersed with a 1.5 μm blazed grating housed in a 1 m monochromator. The signal was detected by a liquid N_2 cooled Ge detector and standard lock-in techniques. Lifetime measurements were made with a faster liquid N_2 cooled Ge detector and digital oscilloscope. Band edge GaN spectra were excited with 2 mW of the 325 nm line of a He–Cd laser. Luminescence was dispersed with a 400 nm blazed grating housed in the same monochromator and detected with a photomultiplier tube. The resolution of the system was at least 1.5 nm and the spectra have not been corrected for system response.

Figure 1 provides the 11 K spectra of the Er^{3+} emission for both the *in situ*-doped and ion-implanted GaN:Er. The spectra have been normalized to the peak emission wavelength for ease of comparison. The peak luminescence intensity of the *in situ*-doped sample is a factor of 5 weaker and the peak wavelength is shifted 2.5 nm compared to the Er^{3+} emission from the implanted sample. The reduced luminescence intensity of the *in situ*-doped sample needs to be investigated further. One possibility is that the excitation mechanism is different between the two samples. Currently, the excitation mechanism is not known, but some researchers have suggested a trap-mediated pathway for Er-implanted GaN.¹⁷ It is also conceivable that the 488 nm light directly excites the Er ions.⁶

The shift in the location of the peak intensity implies that the optically active Er^{3+} center in the two samples is different. This result is supported by the measurement of the 11 K lifetime at the peak emission wavelength. The lifetime of the Er^{3+} emission in the *in situ*-doped sample was determined to be 2.1 ± 0.1 ms. The lifetime of the Er^{3+} emission in the implanted sample was determined to be 2.9 ± 0.1 ms, consistent with previous reports.¹¹ Although the bonding environ-

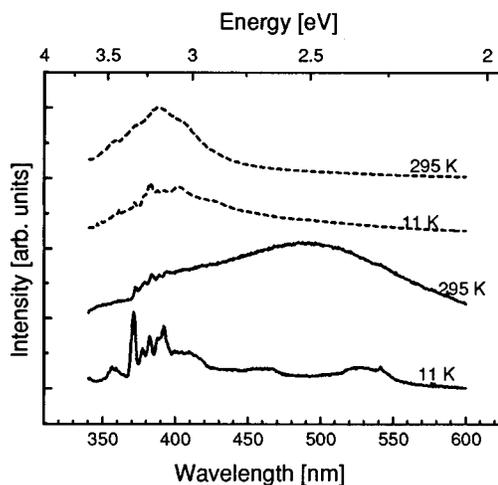


FIG. 2. GaN band edge spectra obtained with 325 nm excitation. The dashed lines are for the *in situ*-doped GaN:Er. The solid lines are for the GaN:Er implanted.

ment of the optically active Er^{3+} ions in both samples is unknown at this time these results indicate that they are different. In the implanted sample, the Er^{3+} is presumably associated with some number of oxygen atoms, however, in the *in situ*-doped sample the associated ligand is unknown since no codopants were intentionally added to the reactor.

The temperature dependence of the Er^{3+} emission intensity in the *in situ*-doped sample could not be determined due to the weak optical signal over the measured temperature range. Above 150 K, the Er^{3+} emission could no longer be detected, however, the peak emission wavelength shifted less than 0.2 nm from 11 to 150 K, which is consistent with emission from the shielded 4*f*-shell electrons. The apparent increased temperature quenching from *in situ*-doped GaN:Er is consistent with what researchers have discovered for GaN:Er grown by metalorganic molecular beam epitaxy.¹⁸ For the implanted sample the peak intensity decreased by a factor of 4 and the integrated intensity decreased by a factor of 1.8 over the temperature range 11–295 K, consistent with previous reports.^{4,8,9,11,12} The peak emission lifetime at 295 K was determined to be 2.3 ± 0.1 ms which is similar to the value reported by Torvik *et al.*⁹

The band edge spectra of the two samples are provided in Fig. 2 for temperatures of 11 and 295 K. Both band edge spectra show a significant amount of structure around 390 nm at 11 K. These spectra indicate that both samples have states within the semiconductor band gap. The difference in band edge emission for the two samples becomes more obvious at a measurement temperature of 295 K. The band edge spectrum of the *in situ*-doped GaN:Er shows only one structure centered at 390 nm. On the other hand, the ion-implanted sample shows a broad defect band centered at 500 nm indicating the presence of deep levels. This result could indicate a reduction in nonradiative pathways from deep level states for the *in situ*-doped sample compared to the ion-implanted sample, however, further work needs to be performed before this can be stated with certainty.

An annealing study was performed on the *in situ*-doped sample to determine if the Er^{3+} luminescence could be improved. The sample was annealed first at 800 °C for 0.5 h in flowing N_2 . Figure 3 shows that the Er^{3+} emission is identi-

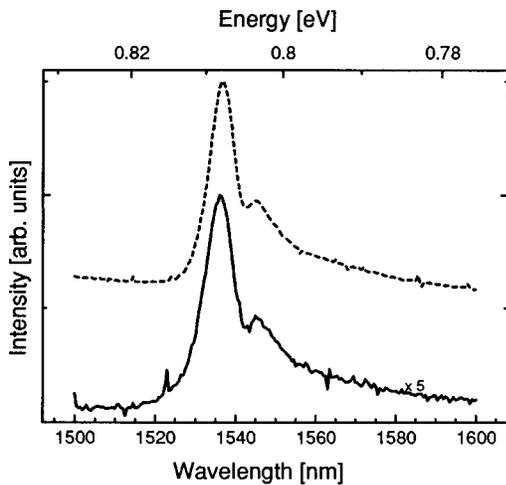


FIG. 3. 11 K photoluminescence spectra of the Er^{3+} emission obtained with 488 nm excitation. The dashed line is for the as-grown *in situ*-doped GaN:Er. The solid line is after annealing at 800 °C in N_2 for 0.5 h.

cal in shape, but a factor of 5 weaker than the as-grown sample. The same sample was then annealed at 800 °C in a NH_3 atmosphere for 0.5 h. The resulting Er^{3+} photoluminescence spectrum is identical to that shown in Fig. 3, however, the intensity returned to approximately the same value as that obtained for the as-grown sample. This result could be interpreted as an effect due to the presence of hydrogen. Hydrogen is known to passivate defects and impurities in GaN. In particular, hydrogen can effectively passivate acceptors in GaN leading to complications in obtaining *p*-type samples. In order to investigate this potential effect of hydrogen, a similar annealing study was performed on the implanted sample, but a similar trend was not discovered. In this case each anneal resulted in continually increasing photoluminescence intensity without affecting the spectrum appearance. One possible explanation for this observation is that the original implant annealing conditions were not optimized, therefore, further annealing optically activated more Er^{3+} ions regardless of the annealing ambient. Implant activation in GaN, in general, has not been studied in detail. Further studies have to be performed in order to determine if passivation or some other mechanism is involved in the reversible intensity changes of the Er^{3+} luminescence for the *in situ*-doped sample.

In summary, we report Er^{3+} luminescence from *in situ*-doped and ion-implanted GaN:Er. The 11 K spectra and lifetime measurements are slightly different than the Er^{3+} emission from an implanted sample indicating a different

optically active center or environment. The 295 K band edge luminescence spectra of the *in situ*-doped sample was free of the broad band luminescence at 500 nm which dominated the implanted sample band edge spectrum. Annealing of the *in situ*-doped GaN:Er in N_2 weakened the Er^{3+} luminescence intensity, however, the intensity returned after subsequent annealing in a NH_3/H_2 ambient. Future work will concentrate on the possible effect of hydrogen on the Er^{3+} luminescence as well as increasing the Er^{3+} intensity in the *in situ*-doped sample.

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