Room-temperature visible and infrared photoluminescence from Pr-implanted GaN films by focused-ion-beam direct write

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Visible and infrared photoluminescence (PL) have been obtained from Pr-implanted GaN films using focused-ion-beam (FIB) direct write utilizing a Pr–Pt liquid alloy ion source. FIB implantation was performed on GaN films grown by molecular-beam epitaxy (MBE), hydride vapor-phase epitaxy, and metalorganic chemical-vapor deposition. After annealing, strong room-temperature emission was observed in the red (at 650 nm) and in the infrared (at several wavelengths including 0.96, 1.3, and 1.9 μm). Essentially identical PL spectra were obtained in the implanted GaN films as in the *in situ* Pr-doped GaN films grown by MBE. © *1999 American Institute of Physics.* [S0003-6951(99)04716-6]

Recently, the success of the incorporation of the rare earth element Er into GaN by ion implantation[1–3] and during growth by hydride vapor-phase epitaxy (HVPE),[4] metalorganic molecular-beam epitaxy,[5] has drawn significant attention because of potential telecommunications applications at near infrared (IR) wavelengths (1.5 μm). In addition, room-temperature visible emission by both photoluminescence[6,7] (PL) and electroluminescence[8,9] have been achieved by solid source molecular-beam epitaxy (MBE) of *in situ* Er-doped GaN. In this case, very strong green emission lines at 537 and 558 nm were observed, in addition to the commonly measured 1.5 μm emission. Focused-ion-beam (FIB) techniques have been used for the maskless and resistless fabrication of a variety of optoelectronic and photonic devices in GaAs and InP based structures.[10,11] The use of Ga^+ FIB to achieve GaN micromilling has been recently reported along with its application to the fabrication of Bragg diffraction mirrors for short cavity lasers.[12] In this letter, we report on the implantation of another rare earth element, namely Pr, into GaN films using FIB direct write. We also compare the optical characteristics of the Pr-implanted GaN to those of *in situ* doped GaN:Pr films grown by MBE.

The praseodymium implantation was performed in a MicroBeam 150 FIB system utilizing a Pr–Pt liquid alloy ion source (LAIS). The Pr–Pt alloy was prepared by mixing praseodymium and platinum at an atomic percent ratio of 87:13. This produces an eutectic alloy with a melting point of 718 °C. Mass spectrum analysis showed that a Pr^{2+} target current of ~200 pA was produced, representing 75% of the total target current. A Pt^+ target current of ~25 pA was also observed. A detailed description of the Pr–Pt LAIS will be published separately.

The Pr^{2+} beam was accelerated to high energy and implantation was carried out at room temperature on GaN films grown by MBE, HVPE, and metalorganic chemical-vapor deposition (MOCVD). After FIB implantation, the samples were annealed under different conditions. PL measurements were performed at room temperature by pumping the samples with a continuous wave He–Cd laser at 325 nm. The He–Cd laser was focused on the sample surface, where the laser power and beam diameter were 12 mW and 200 μm, respectively. The PL signal was collected by a lock-in amplifier and characterized with a 0.3 m Acton Research spectrometer outfitted with a photomultiplier tube detector for ultraviolet (UV)-visible wavelengths and an InGaAs detector cooled to 0 °C for IR. A grating of 1200 grooves/mm with a resolution of 1.67 nm/mm was used for UV-visible wavelengths.

Figure 1 shows the annealing effect on PL intensity for a Pr-implanted GaN film grown on sapphire by MBE. The implanted pattern is a 136 μm×136 μm square. The implantation was performed using a 300 keV Pr^{2+} beam with a target current of 200 pA. The pixel exposure time was 1.14 ms and the pixel size was 0.265 μm×0.265 μm. This results in a dose of $\sim 1\times 10^{15}$ atoms/cm^2. Simulation[13] of these implantation conditions using TRIM'95 calculates a projected

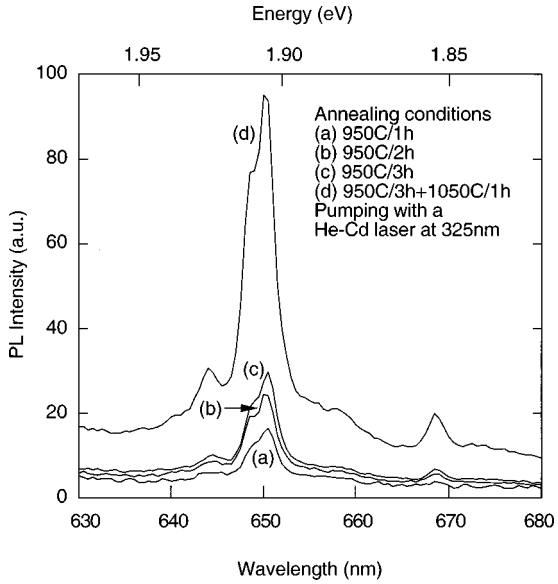

FIG. 1. PL spectra of Pr FIB-implanted GaN films grown by MBE under different annealing conditions (λ_{pump}=325 nm, spectral resolution =0.8 nm).

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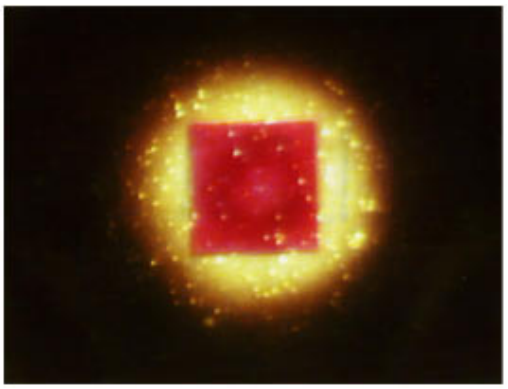

FIG. 2. Red PL from a Pr FIB-implanted GaN film grown on sapphire by MBE. The implanted pattern is a 141 μm×141 μm square. The implantation energy and dose are 290 keV and 4.7×10^{14} atoms/cm^2, respectively. The sample was annealed at 1050 °C for 1 h in Ar after implantation.

range of ~60 nm and a peak concentration of ~1.7×10^{20} atoms/cm^3. The sample was first annealed at 950 °C for 1 h in flowing argon. After this first anneal, the 650 nm peak became discernible. The sample was subsequently annealed at 950 °C for another 2 h, leading to an increase in the peak intensity at 650 nm. The third anneal was carried out at 1050 °C for 1 h resulting in the PL intensity at 650 nm increasing by a factor of 4. In spite of the small implanted pattern size (136 μm×136 μm), the emitted red light intensity was strong enough to be easily seen with the naked eye. Annealing for a fourth and final time at 1050 °C resulted in a reduced PL intensity. This suggests that a one-step annealing at 1050 °C is adequate to optically activate the Pr^{3+} ions implanted in the GaN film. Similar PL spectra were observed from Pr-doped sulfide glasses.[14]

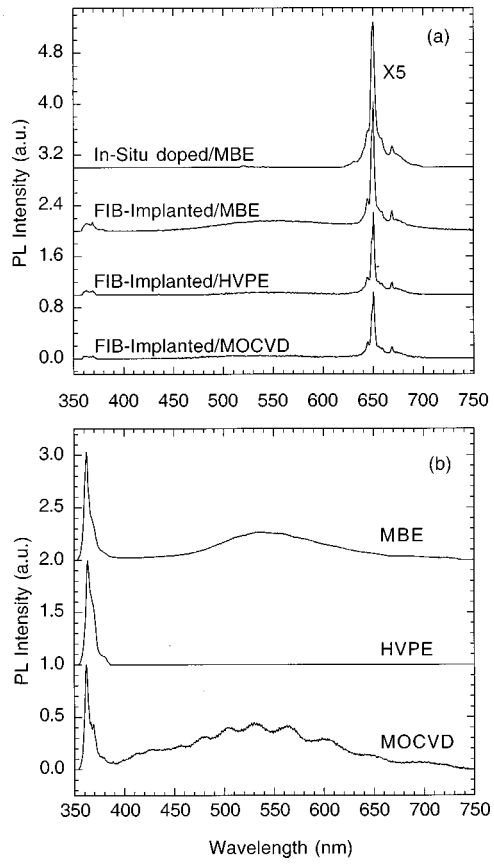

FIG. 3. (a) Visible PL spectra of Pr FIB-implanted GaN films. The doses are 4.7×10^{14}, 1×10^{15}, and 1×10^{15} atoms/cm^2 for MBE, HVPE, and MOCVD samples, respectively. These three samples are annealed at 1050 °C in Ar for 1 h. Also shown in this graph is the PL spectrum of an *in situ* doped GaN/Si:Pr grown by MBE. (spectral resolution=0.8 nm). (b) PL spectra from unimplanted regions of GaN films grown by MBE, HVPE, and MOCVD. Each spectrum is normalized to its peak height value. The band edge (~365 nm) emission intensity in the unimplanted samples is approximately 5×, 20×, and 1× stronger than the red (650 nm) emission for the FIB-implanted MBE, HVPE, and MOCVD samples, respectively. (spectral resolution=0.8 nm).

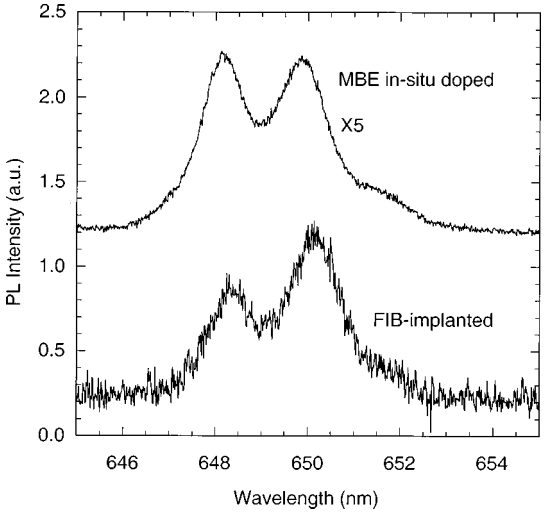

FIG. 4. High resolution scans of the $^3P_0\rightarrow{}^3F_2$ transition of Pr^{3+}. The dose of the FIB-implanted sample is 4.7×10^{14} atoms/cm^2, annealed for 1 h at 1050 °C in Ar. The FWHM of the PL lines at room temperature is ~1.2 nm, which corresponds to ~3.6 meV (spectral resolution=0.08 nm).

Figure 2 shows a GaN region patterned by Pr FIB implantation. The implantation was performed using a 290 keV Pr^{2+} beam for a dose of ~4.7×10^{14} atoms/cm^2. After FIB implantation, the sample was annealed at 1050 °C for 1 h in Ar. Under UV excitation from the He–Cd laser, the implanted region emits red light, while unimplanted surrounding area shows the yellow band emission of GaN.

Pr implantation was also performed on GaN films grown by HVPE and MOCVD. Regions consisting of 141 μm×141 μm squares were implanted on both samples with a dose of 1×10^{15} atoms/cm^2 and a beam energy of 290 keV. Figure 3(a) shows PL spectra from these two samples and that from the Pr-implanted MBE sample (dose=4.7×10^{14} atoms/cm^2). All three samples show strong red emission at 650 nm, which corresponds to the $^3P_0\rightarrow{}^3F_2$ transition of Pr^{3+}. For comparison, the PL spectrum of an *in situ* Pr-doped GaN film (Pr: 10^{18}–10^{20} atoms/cm^3) grown on Si by MBE[15] is also shown in Fig. 3(a). Figure 3(b) contains the PL spectra from unimplanted regions of the three annealed samples. All three samples show similar band edge emission at around 365 nm. By comparing Figs. 3(a) and 3(b), it is apparent that the GaN band edge emission was greatly reduced by the implantation of Pr.

Figure 4 shows a high resolution scan of the $^3P_0\rightarrow{}^3F_2$ transition of the Pr-implanted GaN film grown by MBE on sapphire. After FIB implantation with a dose of 4.7×10^{14} Pr/cm^2 the sample was annealed at 1050 °C for 1 h in Ar. The PL spectrum from an *in situ* Pr-doped GaN film grown on Si by MBE (thickness ~1 μm) is also shown in

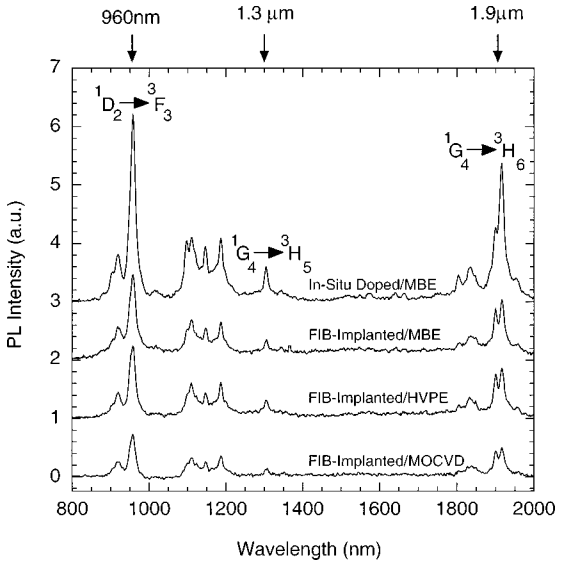

FIG. 5. IR PL spectra of Pr-implanted GaN films. The doses are 4.7×10^{14}, 1×10^{15}, and 1×10^{15} atoms/cm^2 for MBE, HVPE, and MOCVD samples, respectively. The spectra are obtained under identical experimental conditions. (spectral resolution=6 nm).

Fig. 4. The Pr concentration of the *in situ* doped GaN film is estimated to be at the range of $10^{18}-10^{20}$ atoms/cm^3. The data in Fig. 4 were taken under identical experimental conditions and the spectral resolution was 0.08 nm. In general, the two spectra are very similar. The PL intensity of the *in situ* Pr-doped GaN sample is stronger ($\sim5\times$) than that in the FIB-implanted sample, which is expected from the much larger Pr-doped volume which is excited in the former case. For both samples, the full width at half maximum (FWHM) of the 648 and 650 nm lines are $\sim$1.2 nm, which corresponds to 3.6 meV.

Figure 5 shows the base line subtracted infrared PL spectra of three FIB-implanted samples, along with the spectrum from an *in situ* Pr-doped GaN sample grown by MBE. Essentially identical IR PL spectra were obtained. In addition to the commonly observed 1.3 μm line, strong emissions at 960 nm and 1.9 μm were also observed. The PL intensity from the *in situ* Pr-doped GaN sample is three times stronger than that from the FIB-implanted GaN samples, but represents emission from a much larger sample volume.

In summary, we have reported optical emission characteristics of Pr-implanted GaN grown by MBE, HVPE, and MOCVD. After annealing at 1050 °C for 1 h in Ar, strong room temperature emission was observed in the red (at 650 nm) and in the infrared. Essentially identical results were obtained comparing with *in situ* Pr-doped GaN, thus establishing the feasibility of FIB direct write with Pr for GaN light emitting device fabrication.

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