Upconversion luminescence of Er-implanted GaN films by focused-ion-beam direct write

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Upconversion luminescence has been obtained from Er-implanted GaN films by focused-ion-beam (FIB) direct write. FIB implantation was performed on GaN films grown by molecular beam epitaxy, hydride vapor phase epitaxy, and metalorganic chemical vapor deposition. After implantation, the GaN samples were annealed at 1100 °C for 1 h in various ambients (Ar, N_2, and O_2). Strong green upconversion was observed at 523 and 546 nm under red (840 nm) and infrared (1.0 μm) excitation. Upconversion intensity was measured for Er doses ranging from 4.3×10^{12} to 2.4×10^{16} atoms/cm^2. Maximum upconversion intensity at 546 nm was observed at a dose of $1-2\times10^{15}$ atoms/cm^2, which corresponds to an atomic percentage of 0.3%–0.6%. © *1999 American Institute of Physics.* [S0003-6951(99)01539-9]

Recently, the success of the incorporation of the rare earth (RE) element Er into GaN by ion implantation[1–3] and during growth by hydride vapor phase epitaxy (HVPE),[4] metalorganic molecular beam epitaxy (MOMBE),[5] has drawn significant attention because of potential telecommunications applications at near infrared (IR) wavelengths (1.5 μm). In addition, room temperature visible emission from Er in GaN by photoluminescence (PL),[6,7] electroluminescence (EL),[8,9] and cathodoluminescence (CL)[10] has been achieved by solid source molecular beam epitaxy (MBE) *in situ* doping or by ion implantation. 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. Visible, room temperature emission by PL, EL, and/or CL of various other rare earth elements (Pr, Tm, Eu, and Dy) in GaN has also been observed.[10–14] This shows that GaN is an excellent host for the incorporation of rare earth elements in order to produce visible light emission. In this letter, we report on the green upconversion luminescence of Er-implanted GaN films using focused-ion-beam (FIB) direct write.

The erbium implantation was performed in a Micro-Beam 150 FIB system utilizing an Er–Ni liquid alloy ion source (LAIS).[15] The Er^{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 at 1050–1100 °C for 1 h in different gas ambients. This temperature range is chosen because it was shown that an annealing temperature higher than 1000 °C is necessary to optically activate rare earth elements in GaN.[10,12] Upconversion spectra were obtained at room temperature by pumping the sample with two focused continuous wave (CW) InGaAs lasers at 840 nm and 1.0 μm. The maximum pumping power of the 840 nm laser and the 1.0 μm laser on the sample were 270 and 100 mW, respectively. These two lasers were aligned and overlapped on the sample. Both lasers had a beam diameter of 10 μm on the sample. Signals were characterized with a 0.5 m Acton Research spectrometer outfitted with a photomultiplier tube. A grating of 1200 grooves/mm with a resolution of 1.67 nm/mm was used. All measurements were carried out at room temperature.

Figure 1(a) shows the upconversion spectra of Er-implanted GaN films grown by MBE on sapphire and post-implantation annealed under different ambients. Patterns of 51 μm×51 μm squares were implanted on GaN films using a 200 keV Er^{2+} beam with a target current of 100 pA. The

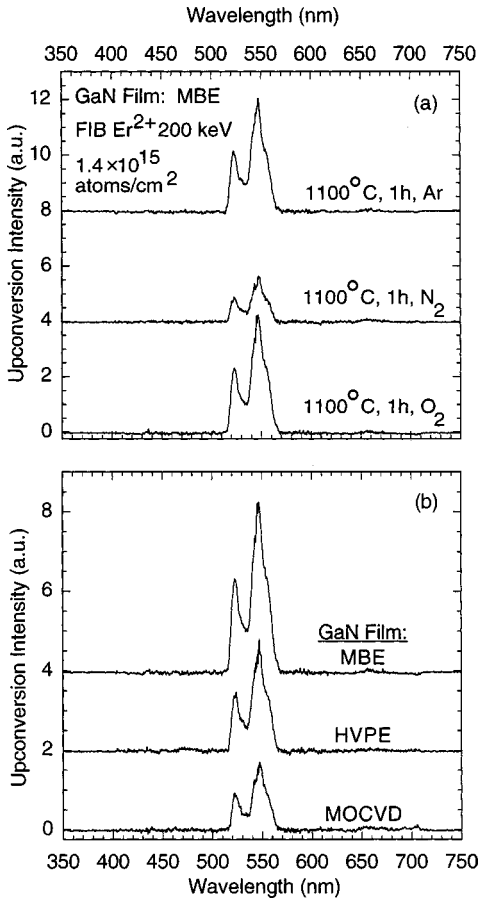

FIG. 1. Upconversion fluorescence of Er FIB implanted GaN films. The implantation energy was 200 keV and the dose was 1.4×10^{15} atoms/cm^2. The spectra were collected by pumping the sample with lasers at 840 nm (270 mW) and 1.0 μm (100 mW). (a) MBE samples under different annealing ambients. (b) GaN films grown by MBE, HVPE, and MOCVD, all annealed at 1100 °C for 1 h in oxygen.

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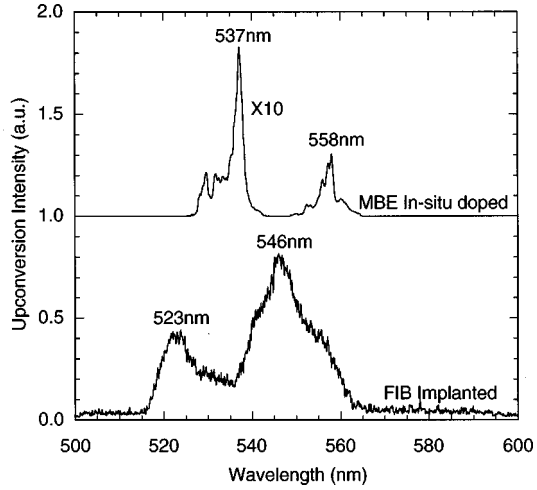

FIG. 2. High resolution scans of the green upconversion luminescence of an Er FIB implanted GaN film and an *in situ* Er-doped GaN film grown by MBE. The FIB implanted sample was annealed at 1100 °C for 1 h in oxygen after implantation. (spectral resolution=0.4 nm)

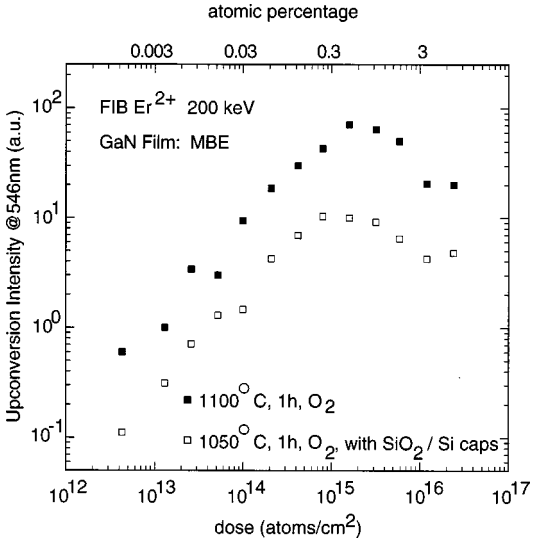

FIG. 3. The upconversion intensity at 546 nm as a function of FIB Er^{2+} dose into a GaN film grown by MBE.

pixel exposure time was 0.46 ms and the pixel size was $0.1\,\mu\text{m}\times0.1\,\mu\text{m}$. This results in a dose of 1.4×10^{15} atoms/cm^2. Simulation[16] of these conditions using transport of ions in matter (TRIM) '95 calculates a projected range of ~38 nm and a peak concentration of $\sim3.7\times10^{20}$ atoms/cm^3 (0.4 at. %). After implantation, the samples were annealed at 1100 °C for 1 h in flowing oxygen, nitrogen, or argon ambients with a gas flow rate of 120 sccm. Figure 1(a) shows that samples annealed in oxygen or argon ambient have stronger upconversion intensity than samples annealed in nitrogen. Similar upconversion spectra have also been reported[17] for Er-doped glasses.

Er implantation was also performed on GaN films grown by HVPE and MOCVD. After FIB implantation, annealing in oxygen was performed. Figure 1(b) compares the upconversion spectra from the HVPE and MOCVD samples to that from the Er-implanted MBE sample. All three samples show strong green emission at 523 and 546 nm.

Figure 2 shows a high resolution scan of the green upconversion of the Er-implanted GaN film grown by MBE on sapphire. The upconversion spectrum from an *in situ* Er-doped GaN film[6] grown on Si by MBE (thickness~$1.5\,\mu$m) is also shown in Fig. 2. Secondary ion mass spectroscopy (SIMS) analysis[18] indicated that the Er concentration of the *in situ* doped GaN film is $\sim5\times10^{20}$ atoms/cm^3, which is nearly the same as the concentration of the implanted sample (3.7×10^{20} atoms/cm^2). The upconversion intensity from the MBE *in situ* doped GaN film is approximately ten times stronger than that from the FIB implanted sample. This is expected because of the much larger Er-doped volume which is excited in the former case. The spectrum also shows that the full width at half maximum (FWHM) of the MBE *in situ* doped sample is much narrower (~2 nm at 537 nm) than the FIB implanted sample (~12 nm at 546 nm). This indicates that residual disorder from the FIB implantation still remains and causes the Er atoms to have varying local environments.

Figure 3 shows the upconversion intensity of FIB implanted GaN films at 546 nm as a function of the Er-implanted dose. To obtain a wide dose range, various square sizes were implanted in GaN films grown by MBE on sapphire. For doses equal to or larger than 8.0×10^{14} atoms/cm^2, squares of $26\,\mu\text{m}\times26\,\mu\text{m}$ were patterned, while the pixel exposure time was varied. For doses less than or equal to 4.2×10^{14} atoms/cm^2, squares of $51\,\mu\text{m}\times51\,\mu\text{m}$ or larger were patterned while the pixel exposure time was also adjusted. This results in a dose range from 4.3×10^{12} to 2.4×10^{16} atoms/cm^2. After FIB implantation, the samples were annealed at 1050 °C (with SiO_2/Si proximity caps) or 1100 °C (no caps) for 1 h in oxygen. The upconversion intensity was measured by positioning the laser beam at the center of the patterned area. Figure 3 shows that the upconversion intensity at 546 nm first becomes discernable at a dose of 4×10^{12} atoms/cm^2. It rises as the dose is increased and reaches a maximum at a dose of $\sim1-2\times10^{15}$ atoms/cm^2. Further increases in Er dose actually result in a decrease of the upconversion intensity. The upconversion intensity of the sample annealed at 1050 °C is weaker than that from the sample annealed at 1100 °C, but both samples show the same trend. Similar effects of the Er concentration on PL were also observed for Er-implanted Si[19] and InP,[20] with maximum PL intensity observed at an Er concentration of 4×10^{17} and 1×10^{18} atoms/cm^3, respectively. It is important to point out that the Er concentration for maximum PL upconversion intensity in our case is 100–200 times larger. The maximum integrated upconversion power measured over the 500–600 nm spectral range was ~40 pW. This was obtained at an Er dose of 1.4×10^{15} atoms/cm^2 with pumping laser power of 270 mW at 840 nm and 100 mW at 1 μm. We believe that adjusting the pumping laser wavelengths will increase the upconversion power.

Figure 4 shows the relevant Er inner shell transition levels, the photon energies of the excitation lasers, and the GaN conduction band edge. The four simplest combinations which can result in the green emission from the $^2H_{11/2}$ and $^4S_{3/2}$ levels based on combinations of two incident photons are: Type I(a) and I(b), Type II(a) and II(b). To determine which combination dominates, the intensity at 546 nm was measured as a function of pump laser power. Figure 5 shows the upconversion intensity at 546 nm as a function of the 840

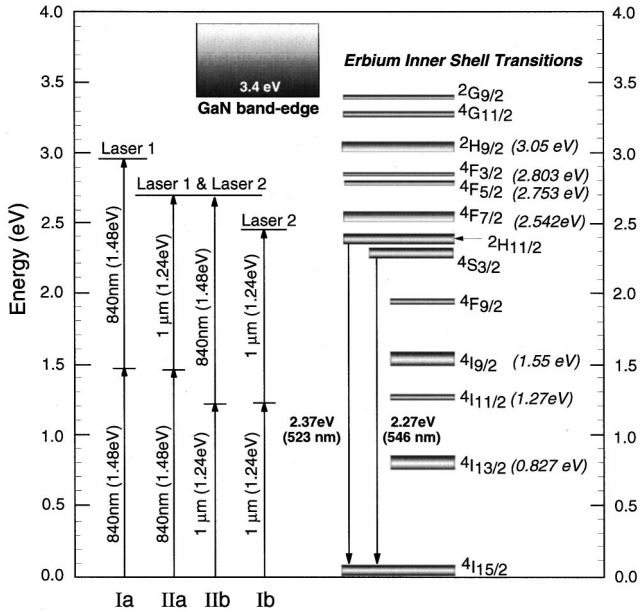

FIG. 4. Inner shell levels of Er^{3+} showing the transitions producing the upconversion emission. Also shown are four possibilities that can result in the green fluorescence.

nm and the 1 μm laser power. From Fig. 5(a), we observe that reducing the 1 μm laser power to zero still allows significant upconversion to occur as the 840 nm laser power is increased. However, reducing the 840 nm laser power to zero essentially extinguishes the upconversion signal at *any* power level of the 1 μm laser. The complementary results are observed in Fig. 5(b). In this case, reducing the 1 μm pump power to zero still produces significant upconversion at nonzero power levels of the 840 nm laser. These results clearly indicate that the upconversion process is mainly accomplished by the absorption of two 840 nm photons (Ia) or one 840 nm photon plus one 1 μm photon (IIa, IIb). The two 1 μm photon combination (Ib) contributes negligibly to the green emission. Figure 5(a) also indicates that when the sample was excited with the 840 nm laser only, the upconversion intensity depends quadratically on the 840 nm laser power. This implies that two 840 nm photons are absorbed to produce one green photon.[21] Clearly the upconversion processes which utilize the 840 nm excitation appear to benefit from the efficient excitation from the ground state to the $^4I_{9/2}$ level. This conclusion seems to be valid for both types I(a) and II(a). Further investigations are necessary to fully understand the upconversion mechanism.

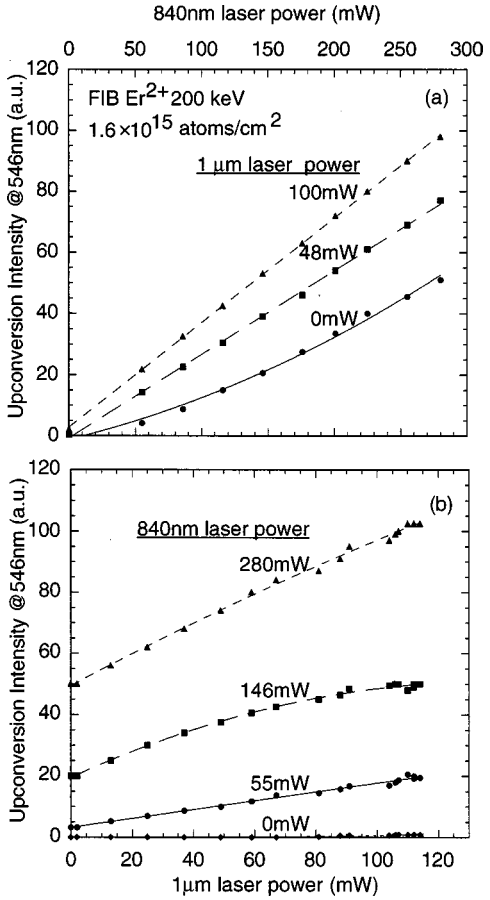

FIG. 5. Upconversion intensity at 546 nm as a function of laser excitation pump power: (a) 840 nm laser; (b) 1 μm laser.

In summary, we have obtained room temperature upconversion luminescence from Er-implanted GaN films by FIB direct write. Nearly identical results were obtained from Er-implanted GaN films grown by MBE, MOCVD, and HVPE. Maximum upconversion intensity at 546 nm was obtained at a dose of $1-2\times10^{15}$ atoms/cm^2, which corresponds to an atomic percentage of 0.3%–0.6%. The upconversion process is driven by the absorption of two 840 nm photons or one 840 nm photon plus one 1 μm photon.

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