Optical and magnetic behavior of erbium-doped GaN epilayers grown by metal-organic chemical vapor deposition

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The authors report on the optical and magnetic properties of GaN epilayers, grown by metal-organic chemical vapor deposition, with *in situ* Er doping at concentrations up to $\sim 10^{21}$ cm^{-3}. Using ultraviolet laser excitation, all samples exhibited photoluminescence near 1540 nm with the integrated intensity approximately proportional to the Er concentration. Data from superconducting quantum interference device measurements indicated room temperature ferromagnetic ordering in all Er-doped GaN epilayers. The saturation magnetization in these samples also followed a nearly linear fit to the Er concentration. X-ray diffraction spectra did not reveal evidence of any second phases over this range of Er concentrations. © *2007 American Institute of Physics*.
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A strong research activity exists in the properties of rare-earth (RE) doped III-N semiconductors for potential applications including full color displays and devices for telecommunications.[1] The excited states of RE elements (such as Gd, Tm, Eu, and Er) lead to sharp emission lines from the ultraviolet (UV) through the visible to the infrared (IR).[2] Due to the wide band gap energies of GaN, AlN, and their alloys, emissions of higher energy RE transitions can be observed that are otherwise absorbed in narrow band gap semiconductors.[3,4] Doping of GaN with either Eu or Gd ions has also yielded room temperature (RT) ferromagnetic ordering, although the mechanism is still far from clear.[5–8] However, concentrations of RE ions needed to induce ferromagnetism in GaN are significantly lower than those required with transition metals (TMs). Whereas doping of GaN with Mn or Cr normally requires concentrations on the order of 5×10^{20} cm^{-3} to yield ferromagnetism, concentrations of only 10^{16}–10^{18} cm^{-3} for Gd or $\sim10^{19}$ cm^{-3} for Eu are sufficient.[9,10] The lower doping concentrations lead to less compromise in material quality and allow the host nitride semiconductor to be codoped with conventional shallow level *n*-type dopants to control the conductivity.[11] In addition, use of wide band gap semiconductors as the host material has been shown to reduce the thermal quenching of the characteristic intra-4*f* shell atomic transitions of the RE ions.[12–14] Consequently, III-N semiconductors doped with RE ions appear as promising material candidates for producing magnetic and optical functionalities on a single chip. In this letter, we report on the synthesis of Er-doped GaN by metal-organic chemical vapor deposition (MOCVD) and the resulting optical and magnetic properties of the thin films.

The element Er is a member of the lanthanide rare earth series and possesses 11 electrons in the 4*f* shell. In the trivalent charge state (Er^{3+}) these 4*f* electrons are shielded from the host environment by completely filled 5*s* and 5*p* electronic shells.[2] The 4*f* energy levels are largely independent of host material and transitions between these levels lead to wavelength-stable luminescence. In particular, transitions between the first excited manifold ($^4I_{13/2}$) and the ground state ($^4I_{15/2}$) give rise to IR emissions near 1.54 μm. Due to the importance of this wavelength region for optical communications, Er doping of silica fibers, as well as various semiconductors, has received widespread research attention.[1–4,12–19] In addition, following Hund's rule, there are three unpaired 4*f* in Er atoms that can contribute to ferromagnetic ordering. Bang *et al.* investigated the magnetic properties of GaN thin films doped with Er but did not observe definitive ferromagnetic behavior.[17]

The Er-doped GaN samples examined in this study were grown by MOCVD in a horizontal reactor on (0001) *c*-plane sapphire substrates.[18] Trimethylgallium was used for the Ga source, blue NH_3 was used as the *N* source, and tris(2,2,6,6-tetramethyl-3,5-heptanedionato)erbium, was the metal-organic precursor used for the *in situ* Er doping. Growth of the epilayers began with a thin GaN buffer layer, followed by a 1.2 μm GaN epilayer template, and then by a 0.5 μm Er-doped GaN layer. The growth temperature for the GaN template and Er-doped GaN layer was 1040 °C. The Er concentration was varied by controlling the Er precursor flux during growth. This procedure produced thin films with Er concentrations in the range of $(2-10)\times10^{20}$ cm^{-3} as determined by secondary-ion mass spectroscopy calibration measurements. The electrical properties were determined by van der Pauw Hall effect measurements and found to be comparable to those of high-quality undoped MOCVD GaN films. The electron mobility was $\sim$200 cm^2/V s, electron concentration $\sim2\times10^{17}$ cm^{-3}, and the resistivity $\sim$0.2 Ω cm. These properties were relatively unchanged with increasing Er concen-

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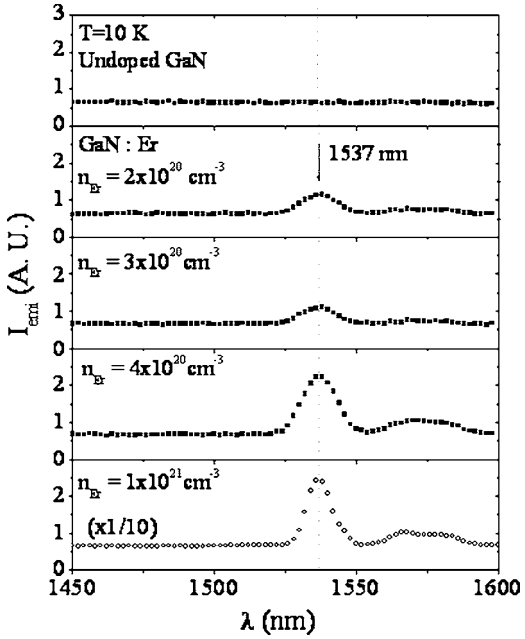

FIG. 1. Infrared PL spectra taken at 10 K from GaN epilayers having Er concentrations in the range of $(2-10)\times10^{20}$ cm^{-3}. PL from an undoped control sample is also shown.

tration (n_{Er}).[19] The samples were also characterized by powder x-ray diffraction (XRD) measurements to ascertain crystal quality. All the samples were of high crystallinity and there was no indication of second phase formation, even with Er doping $\sim10^{21}$ cm^{-3}.

Using UV lasers, photolvminescence (PL) measurements were made with a 1.3 m monochromator equipped with an InGaAs detector. Results from PL measurements taken at 10 K using an excitation wavelength of 263 nm are shown in the panels of Fig. 1. The PL spectra cover the range of 1450–1600 nm and are displayed as function of n_{Er}. In the top panel, the PL spectrum from an undoped GaN sample is also shown. The PL measurements taken at 10 K yielded spectra with a dominant peak at ~1537 nm that is due to the intra-4f $^4I_{13/2}\rightarrow{}^4I_{15/2}$ transition of the Er^{3+} ions and whose peak intensity was proportional to n_{Er}. Even at a value of $n_{Er}\sim10^{21}$ cm^{-3} there was no indication of concentration quenching of the PL signal. As the measurement temperature was increased to RT, several emission peaks near 1540 nm appeared in the PL spectra indicating the crystal-field splittings in the $^4I_{13/2}$ and $^4I_{15/2}$ states. In Fig. 2(a), the evolution of these peaks is displayed for the sample with $n_{Er}\sim4\times10^{20}$ cm^{-3}. The PL spectra were taken with an Ar ion laser and are offset on the same scale for clarity. The thermal quenching behavior of the normalized integrated PL intensity (I_{emi}) for samples with $n_{Er}\sim0.4$ and 1.0×10^{21} cm^{-3} is shown in Fig. 2(b).

Magnetic measurements were taken using a Quantum Design magnetic properties measurement system superconducting quantum interference device (SQUID) magnetometer. In all cases, the magnetic field was applied vertical to the sample surface which is the easy axis of magnetization.[6] Diamagnetic properties of the substrate and holder were subtracted out and the data normalized to sample volume. Each of the GaN:Er epilayers displayed RT hysteretic behavior consistent with ferromagnetic ordering. The magnetization (M) data as a function of temperature T of the sample having

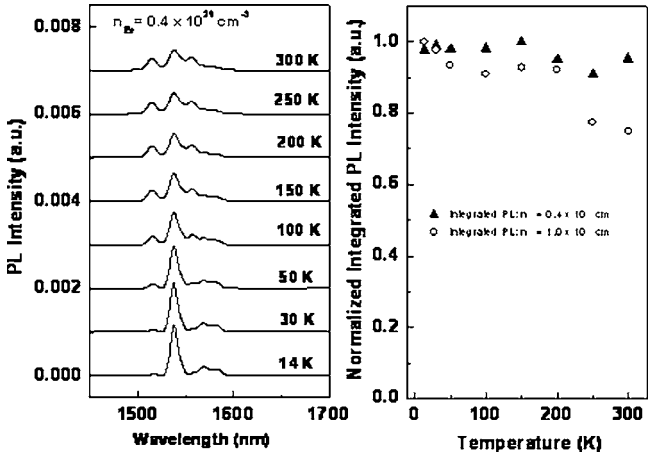

FIG. 2. (a) PL spectra at indicted temperatures taken from the epilayer having an Er concentration of $\sim4\times10^{20}$ cm^{-3}; (b) Thermal quenching of the integrated PL intensity for samples with n_{Er} of 0.4×10^{21} cm^{-3} and 1.0×10^{21} cm^{-3}.

$n_{Er}\sim10^{21}$ cm^{-3} are summarized in Fig. 3. The data points show the results of the zero-field-cooled (ZFC) and field-cooled (FC) SQUID measurements done with an applied magnetic field of 200 Oe. Previous reports have shown the importance of crystalline quality in achieving strong magnetization in TM-doped nitrides.[20] In the present experiments, the "blocking temperature" (T_B), the temperature at which the ZFC/FC curves meet, is clearly above 300 K. This is further evidence of the high quality of the GaN:Er epilayers grown by MOCVD. The samples displayed hysteresis at 300 K with coercivity of ~100 G. Magnetization measurements were also performed on an undoped GaN sample to eliminate the possibility that spurious TM impurities might be responsible for the magnetic response. No magnetic hysteresis was observed in the undoped sample providing evidence that Er doping is responsible for the observed magnetization.

The two panels in Fig. 4 summarize the dependence of I_{emi} and the saturation magnetization (M_S) on the Er concentration. In the top panel data points for the I_{emi} at 1.54 μm are plotted versus n_{Er}. While the PL signal was not very strong at lower concentrations, the I_{emi} increases monotonically with n_{Er} at both 10 and 300 K. The straight lines are

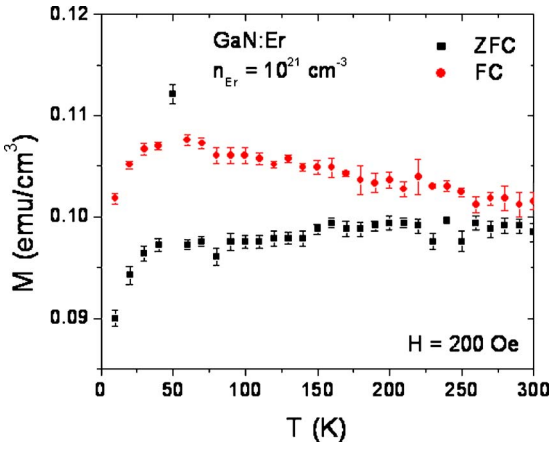

FIG. 3. SQUID measurements as a function of temperature from GaN epilayer with an Er concentration of $\sim10^{21}$ cm^{-3}, in an applied field of 200 Oe. Field-cooled and zero-field-cooled magnetization data points are shown.

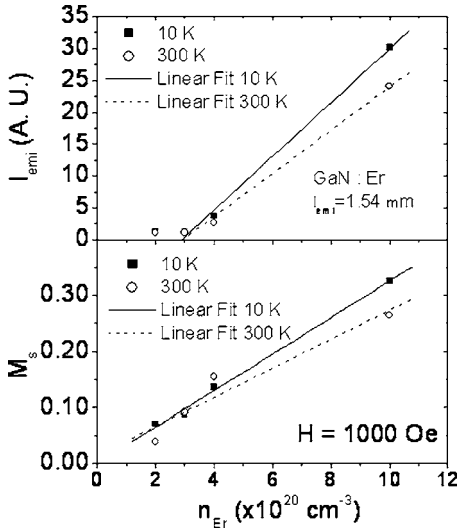

FIG. 4. Plots of the measured integrated PL intensity at 1.54 μm (top panel) and the saturation magnetization (bottom panel) vs Er concentration.

drawn as a guide for the eye. For the sample with $n_{\mathrm{Er}} \sim 10^{21}$ cm^{-3}, the value of I_{emi} at 10 K is approximately 20% than that at RT due to thermal quenching of the luminescence, see Fig 2(b). The high level of doping of this sample may have resulted in point defects or interstitial ions that produced the observed thermal quenching. For lower Er concentrations, thermal quenching of the luminescence was negligible and within experimental error.

In the bottom panel of Fig. 4, the dependence of M_S on n_{Er} is displayed indicating a similar behavior over the range of Er concentrations. The value of M_S, for the sample with $n_{\mathrm{Er}} \sim 10^{21}$ cm^{-3}, is greater at 10 K than at 300 K. The increase in M_S may be due to a more effective ordering of the $4f$ electrons at cryogenic temperatures and to a decrease in the average spacing between Er ions in the lattice. It is also possible that the defects that led to thermal quenching in this sample may also be responsible for the enhanced correlation of $4f$ electrons at 10 K. The M_S values for the other samples with lower Er concentrations are nearly the same at both temperatures.

The M_S data also indicate that the average magnetic moment per Er ion is less than $0.1\mu_B$ for each of the GaN:Er samples. This value is nearly constant for the different Er concentrations and is much less than that found for Eu or Gd in our previous experiments.[9,10]

In summary, we have shown that Er-doped GaN epilayers grown by MOCVD exhibit both luminescence and hysteric behavior. All of the samples examined in this study displayed PL near 1540 nm and ferromagnetic ordering at RT. It should be noted that the GaN:Er epilayers were *n* type and had good electrical properties. Based on XRD measurements, no second phases were present in these samples. Consequently, these findings are not easily accommodated by the theoretical models that have been put forward, primarily for ferromagnetism due to TM doping of GaN semiconductors.[21,22]

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