Optical and magnetic properties of Eu-doped GaN

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GaN films were doped with Eu to a concentration of ~0.12 at. % during growth at 800 °C by molecular beam epitaxy, with the Eu cell temperature held constant at 470 °C. All samples were postannealed at 675 °C. The films exhibited strong photoluminescence (PL) in the red (622 nm) whose absolute intensity was a function of the Ga flux during growth, which ranged from 3.0×10^{-7} to 5.4×10^{-7} Torr. The maximum PL intensity was obtained at a Ga flux of 3.6×10^{-7} Torr. The samples showed room temperature ferromagnetism with saturation magnetization of ~0.1–0.45 emu/cm^3, consistent with past reports where the Eu was found to be predominantly occupying substitutional Ga sites. There was an inverse correlation between the PL intensity and the saturation magnetization in the films. X-ray diffraction showed the presence of EuGa phases under all the growth conditions but these cannot account for the observed magnetic properties. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2358293]

There is continued strong interest in the properties of rare-earth-doped wide band gap nitrides for their potential application in optoelectronic devices such as visible lasers that can be grown on Si substrates.[1–20] In particular, the large band gaps of GaN, AlN, and their alloys allow emission of higher energy rare earth transitions that are otherwise absorbed in smaller band gap host materials such as GaAs. These materials may have application in visible displays or in white light systems that employ color-combining techniques. Rare earth doping of GaN with Eu and Gd has also been reported to produce ferromagnetism, although the mechanism is far from clear.[21–26] Several groups have suggested that there is long range polarization of the area surrounding each Gd atom.[23,24,27] Dalpian and Wei[27] further suggested that the phenomenon requires shallow donor impurities such as oxygen to occupy f states created by the Gd below the conduction band. However, there is a significant difference in the dopant concentrations needed to induce ferromagnetism in GaN between rare earths and the more conventional transition metals such as Mn. In the latter case, concentrations of 3–5 at. % are typically required and this is well above the solid solubility, requiring use of low growth temperatures or nonequilibrium incorporation methods such as ion implantation. By comparison, concentrations of 10^{16}–10^{18} cm^{-3} of Gd and Eu appear sufficient to induce ferromagnetism and correspondingly large magnetic moments. This has the advantage that there is less compromise in the material quality through the use of lower impurity levels and the material may be codoped with conventional shallow level dopants to control the conductivity. Since the rare earth dopants may be optically active in these materials, magnetic and optical functionalities on a single chip may be possible.

In this letter we report on the synthesis of Eu-doped GaN by molecular beam epitaxy (MBE) and the optical and magnetic properties of the resulting films. Strong red (622 nm) photoluminescence is obtained along with signatures of ferromagnetism that do not appear to result from second phase formation.

The samples were grown by MBE on c-plane sapphire substrates. A low temperature, 50 nm thick AlN buffer was followed by growth of ~0.5 μm of GaN:Eu at 800 °C with a Eu cell temperature of 470 °C. The Ga flux during growth was varied from 3.0×10^{-7} to 5.4×10^{-7} Torr by controlling the Ga cell temperature in the range of 860–890 °C. The samples were capped with an additional 50 nm of low temperature AlN and annealed at 675 °C for 100 min. This produces a Eu concentration in the range of 0.12 at. %, as determined by Rutherford backscattering.[28] This is a much lower concentration than used in previous work (2 at. %).[22] Previous measurements have also shown the presence of a significant concentration of oxygen in the samples, which tends to increase the population of the +3 valence state.[9] The samples were insulating and were characterized by room temperature photoluminescence (PL) measurements using a HeCd laser (325 nm) as an excitation source and also by x-ray diffraction (XRD) measurements in a powder system. We also performed some preliminary θ-2θ measurements using a double-crystal system. Magnetic measurements were taken up to room temperature (300 K) with a Quantum Design magnetic properties measurement system superconducting quantum interference device magnetometer. The magnetic field was applied vertical to the sample surface in all cases, the easy axis of magnetization.[22] The diamagnetic properties of the substrate and holder were subtracted out and the data normalized to sample volume.

The PL spectra from the GaN:Eu samples are shown in Fig. 1 as a function of the Ga flux during growth. The spectra show a strong dominant emission at 622 nm due to the intra-atomic transitions inside the $4f$ shell of Eu^{3+} ions ($^5D_0$-$^7F_2$

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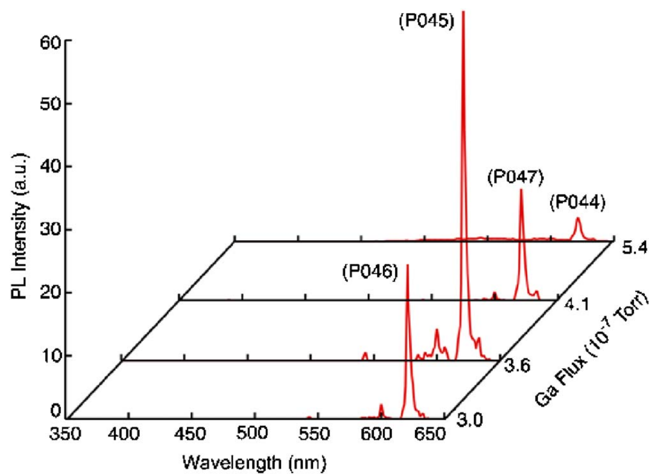

FIG. 1. (Color online) PL spectra at 300 K from Eu-doped GaN samples grown with different Ga fluxes.

transition).[22] The less dominant transition around 599 nm is attributed to Eu^{3+} $4f$ inner shell transitions from $^5D_0$ to $^7F_1$.[15] This is consistent with previous reports that show a correlation between the 622 nm emission and a majority of the Eu ions being in the 3+ state in the GaN,[22,29] with the Eu occupying substitutional Ga sites as determined by extended x-ray absorption fine structure measurements.[29] Note that the PL emission intensity is a maximum at lower Ga fluxes, consistent with the Eu occupying Ga sites. While the III-nitrides have proven quite successful for fabrication of blue and green light emitting devices, realization of red devices has been less successful due to the difficulties associated with the synthesis of the high-In-content InGaN needed to achieve red emission. An attractive alternative may be the use of Eu-doped GaN, whose emission wavelength is host-material insensitive. GaN is an attractive host for optical centers as its wide band gap has been shown to reduce thermal quenching in Er^{+3}-doped material. This reduction in quenching allows efficient operation of Er-doped material at room temperature[15–18] and should offer the same benefit for Eu^{3+}.

Figure 2 shows the magnetization (M) versus field (H) behavior at 300 K for the Eu-doped sample grown with the lowest Ga flux $(3\times10^{-7}$ Torr). Hysteretic behavior is clearly observed, consistent with ferromagnetism. Other possible explanations for hysteretic M vs H behavior that are remotely possible include super-paramagnetism and spin-glass effects. These films also appear to have Curie temperatures (T_C) around room temperature, as shown from the lack of closure between the field-cooled and zero-field-cooled lines in the magnetization vs temperature curves at the bottom of Fig. 2. Magnetization measurements were also performed on undoped GaN samples to eliminate the possibility that spurious transition metal impurities might be responsible for the magnetic response. These exhibited no magnetic hysteresis, showing that the Eu doping is responsible for the observed magnetization.

Figure 3 shows the saturation magnetization and PL intensity at 300 K as a function of the Ga flux during growth of the GaN:Eu. There is an inverse correlation between the two parameters and the 300 and 10 K magnetizations roughly track each other. The PL intensity is a maximum at moderate Ga fluxes, as discussed above. Previous reports have suggested that the ferromagnetism in Eu-doped GaN is

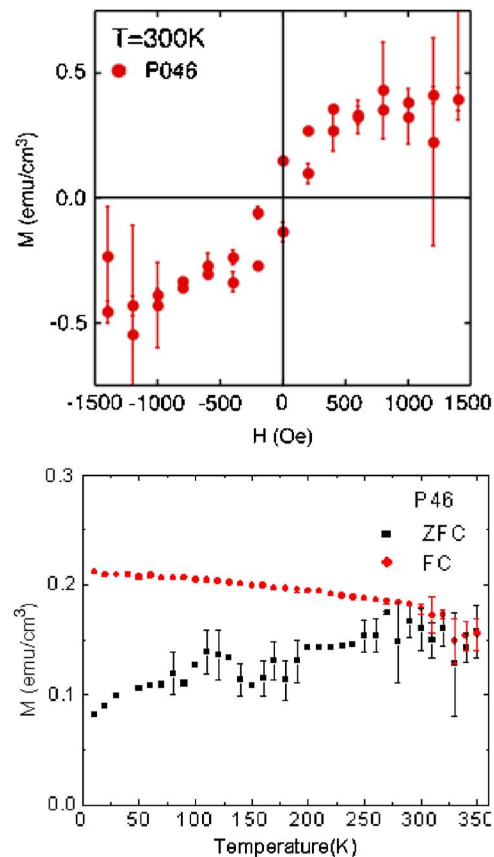

FIG. 2. (Color online) 300 K magnetization vs field curve from Eu-doped GaN grown with a Ga flux of 3.6×10^{-7} Torr (top) and field-cooled and zero-field-cooled magnetizations as a function of temperature (bottom).

due to Eu^{2+} ions because of their large total angular momentum in the ground state, while the Eu^{3+} would lead to paramagnetism.[22] In this scenario, the higher population of the trivalent states at moderate Ga fluxes would correlate with a lower saturation magnetization, as observed. The minima/maxima in Fig. 3 might be explained as follows. The $+2/+3$ ratio decreases with increasing Ga flux. However, as the Ga flux increases (we are always in N-rich growth conditions), the Eu gets increasingly tied up as Eu–Ga phases, leaving less substitutional Eu. The Eu that remains prefers to be increasingly +3, enhancing the optical activity over the

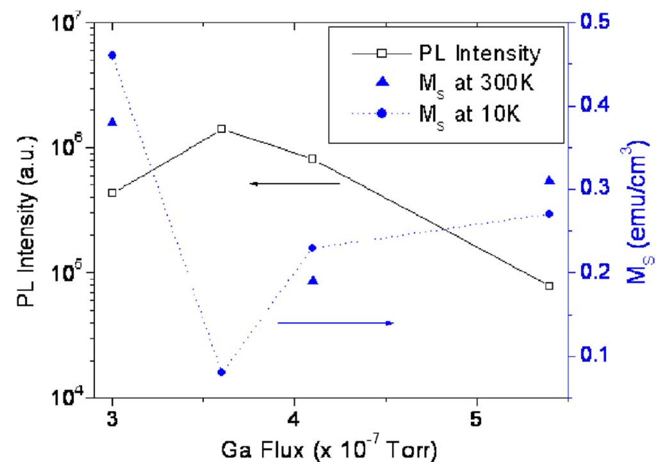

FIG. 3. (Color online) PL intensity at 300 K and saturation magnetization at a field of 1500 Oe at both 10 and 300 K from Eu-doped GaN as a function of Ga flux during growth.

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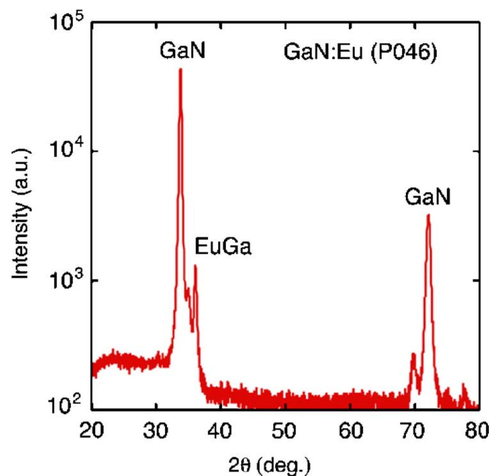

FIG. 4. (Color online) XRD spectrum from Eu-doped GaN grown with a Ga flux of 3.6×10^{-7} Torr.

magnetic activity. The Eu–Ga phases are only weak antiferromagnets, and would be well into paramagnetism for the Fig. 3 measurements at 300 K, and not contributing to any remaining ferromagnetism. A spatial variation in Eu^{3+}/Eu^{2+} concentration ratio in GaN has previously been noted from resonant photoemission measurements.[30] The saturation magnetization in our films is comparable to previous reports even though the Eu concentration is approximately a factor of 16 lower.[22]

Figure 4 shows the XRD spectrum from Eu-doped GaN grown with the lowest Ga flux. We observe the presence of a Eu–Ga phase in addition to the usual GaN peaks. Similar results were obtained for all of our samples. In analogy with the case of Gd in GaN (Ref. 31) and the heat of formation of the respective compounds,[32,33] it might be expected that the reaction $Eu+GaN \rightarrow Ga+EuN+Ga_xEu_yN$ may occur and that the Eu can then form alloys of Eu_xGa_y. Our double-crystal measurements show that at least two different EuGa phases (EuGa and $EuGa_2$) are present. There may be others present below the concentration limit of our system, but none of the Eu–Ga phases are ferromagnetic at high temperatures. Indeed, the respective Néel temperatures are 18 K (EuGa), 22 K ($EuGa_2$), 10–15 K ($EuGa_4$), 23 K (Eu_3Ga_8), and 33 K (Eu_5Ga_8).[34,35] Bulk Eu has a Néel temperature of 90 K, while there are no EuN phases with high Curie temperatures (at 77 K EuN is paramagnetic).[36] In addition, the magnetic semiconductor EuO has a Curie temperature of ~77 K,[32] so it does not appear to be a factor in the observed magnetic properties, while Eu_3O_4 has a Curie temperature of 7.8 K and Eu_2O_3 is paramagnetic.[37]

In conclusion, Eu-doped GaN shows both strong red emission at 622 nm from the $^5D_0 \rightarrow {}^7F_2$ transition of Eu^{+3} and hysteretic behavior in the field dependence of magnetization, consistent with the presence of a ferromagnetic phase. This material appears very promising for multifunctional devices with both optoelectronic and magnetic functions.

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