Blue emission from Tm-doped GaN electroluminescent devices

A. J. Steckl,[a] M. Garter, D. S. Lee, J. Heikenfeld, and R. Birkhahn
Nanoelectronics Laboratory, University of Cincinnati, Cincinnati, Ohio 45221-0030

(Received 27 April 1999; accepted for publication 23 August 1999)

Blue emission has been obtained at room temperature from Tm-doped GaN electroluminescent devices. The GaN was grown by molecular beam epitaxy on Si(111) substrates using solid sources (for Ga and Tm) and a plasma source for N_2. Indium–tin–oxide was deposited on the GaN layer and patterned to provide both the bias (small area) and ground (large area) transparent electrodes. Strong blue light emission under the bias electrode was observable with the naked eye at room temperature. The visible emission spectrum consists of a main contribution in the blue region at 477 nm corresponding to the Tm transition from the $^1G_4$ to the $^3H_6$ ground state. A strong near-infrared peak was also observed at 802 nm. The relative blue emission efficiency was found to increase linearly with bias voltage and current beyond certain turn-on levels. © *1999 American Institute of Physics.* [S0003-6951(99)05641-7]

The development of compound semiconductor-based light emitting diodes (LEDs) covering the entire visible spectrum has been under way for almost three decades.[1] For the past decade, attention has focused on GaN and related InGaAlN alloys whose composition was varied to achieve the suitable band gap for producing the desired emission color.[2,3] We are developing an alternative approach to producing GaN-based LEDs which could cover the visible (and infrared) spectrum utilizing the doping of GaN with luminescent rare earth (RE) species. In our approach the GaN host material does not require alloying with either InN or AlN, but rather the RE atoms are chosen for doping based on the energy of photon emission from their inner shell levels. We have recently shown that RE-activated photoemission in GaN can produce green[4–7] (based on Er doping) and red[8] light (based on Pr doping), as well as near-infrared (IR) emission[9] (using either Er or Pr doping). In this letter, we present a blue electroluminescent device (ELD) based on RE-doping of GaN, utilizing the rare earth element thulium (Tm). We have selected Tm because it is known to have an inner shell transition corresponding to blue emission and to be a very efficient luminescing species in a variety of host materials, including, among others, ZnS,[10] ZnO,[11] YAG,[12] fluorozirconate,[13] zinc borosulphate,[14] and fluorophospate[15] glasses.

Tm-doped GaN films were grown in a Riber molecular beam epitaxy (MBE)-32 system on 2 in. *p*-Si (111) substrates. Solid sources were employed to supply the Ga (7N purity) and Tm (3N) fluxes, while an SVTA radio frequency (rf)-plasma source was used to generate atomic nitrogen. For the work reported here, a GaN buffer layer was first deposited for 10 min at a temperature of 600 °C, followed by GaN growth at a temperature of approximately 800 °C. The growth conditions were as follows: N_2 flow rate of 1.5 sccm at a plasma power of 400 W, Ga cell temperature of 870 °C, and Tm cell temperature of 560–570 °C. GaN:Tm films with thickness of ~ 1 μm were grown in 1 h. The Tm concentration in the GaN layer is estimated to be $\sim 10^{19}$–$10^{20}/\mathrm{cm}^3$, based on the vapor pressure at the evaporation temperature and comparison with similar Er-doped GaN growth.

To fabricate ELDs on the GaN:Tm we utilized transparent and conducting metal electrodes of indium–tin–oxide (ITO). The ITO contacts were formed using rf-sputtering in conjunction with a liftoff process. The ITO target had a composition of 90% In_2O_3 and 10% SnO_2. A deposition rate of $\sim$85 Å/min was obtained by sputtering at a pressure of 3.5 mTorr with 100 W of rf power [which resulted in a direct current (dc) bias of -212 V]. The ITO film was $\sim$5100 Å thick and had an as-deposited sheet resistance of 40 Ω/sq. Annealing in N_2 for 2 min at 450 °C reduced the sheet resistance to $\sim$8 Ω/sq. The optical transmission of the ITO film was measured separately. At the main wavelengths of interest, transmission values of $\sim$86% and $\sim$83.5% were obtained at wavelengths of 480 and 800 nm, respectively. Electroluminescence data were collected using Acton Research and Ocean Optics fiber optic spectrometers. All measurements reported were made at room temperature.

Examples of blue emission from GaN:Tm ELDs are seen in Fig. 1. In Fig. 1(a), the ring geometry ELD with a small area of 7.65×10^{-4} cm^2 requires only 1–2 mA to produce blue emission visible with the naked eye under normal ambient lighting conditions. The photograph was taken under bias conditions of 83.4 V and 7.13 mA. Emission from a larger device (with an area of 0.125 cm^2) is shown in Fig. 1(b) operated under bias conditions of 55 V and 101 mA. In both cases the emitting electrode was positively biased. Reversing the bias polarity also produced blue emission (from the same physical region), but with a lower intensity. While variations in emission intensity and electrical characteristics were observed depending on the location of the device on the substrate, the results presented below are representative.

The optical and electrical characterization of GaN:Tm ELDs utilized the ring devices. A typical EL spectrum is shown in Fig. 2 for an ELD operated at a bias of 116 V and 1.03 mA. The spectrum extending from 450 to 850 nm includes two major lines: (a) in the blue at 477 nm and (b) in the near infrared (IR) at 801 nm. As discussed in more detail below, the intensities of the blue and IR emission lines are

[a]Electronic mail: a.steckl@uc.edu

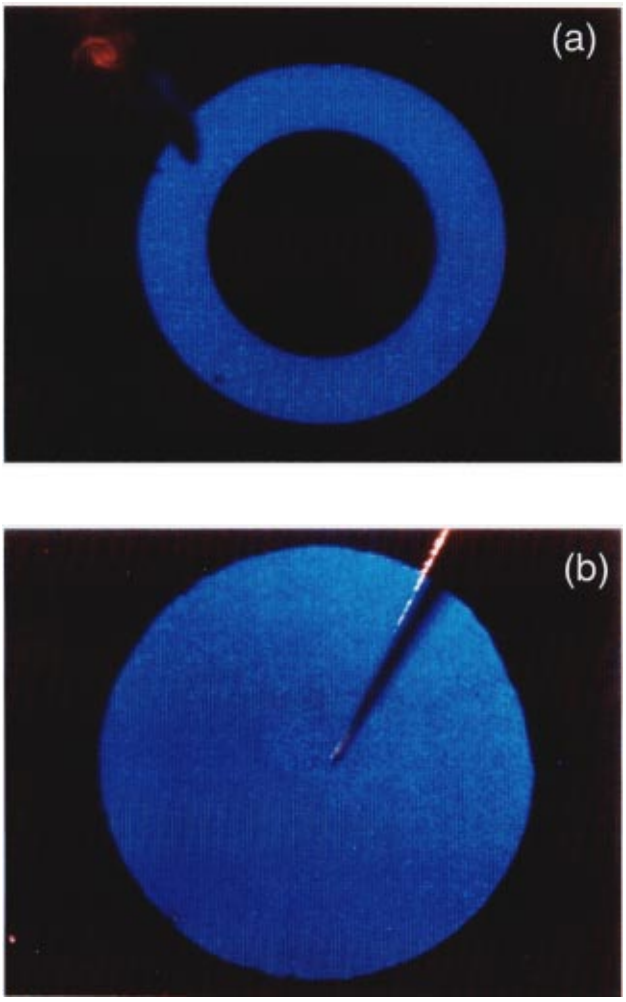

FIG. 1. Blue emission from ITO/GaN:Tm ELDs: (a) ring structure, area of 7.65×10^{-4} cm^2; ring width of 75 μm; bias conditions of 83.4 V and 7.13 mA; (b) dot structure with 0.125 cm^2 area; dot diameter of 4 mm; bias conditions of 55 V and 101 mA.

approximately equal. The linewidths of the 477 and 801 nm peaks had full widths at half maximum (FWHM) of 7.5 and 9.86 nm, corresponding to 40.9 and 19.1 meV, respectively. For comparison, we have previously reported[6,7] a FWHM of 6 nm (25.8 meV) for the 537 nm green EL line in GaN:Er and a FWHM of 7.4 nm (21.7 meV) for the 650 nm red EL line in GaN:Pr. A similar emission spectrum was reported[16] from Tm-implanted GaN utilizing cathodoluminescence. However, in that case the blue emission was much smaller

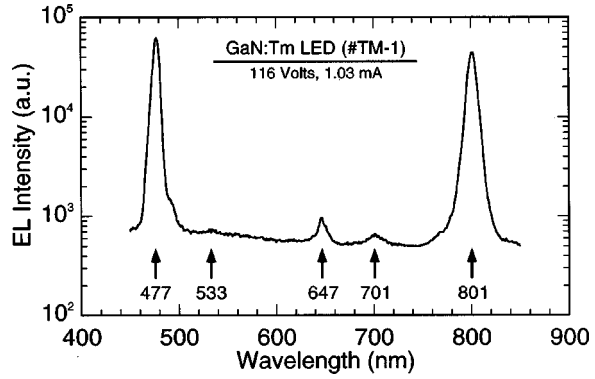

FIG. 2. Room temperature, visible EL spectrum of GaN:Tm ELD.

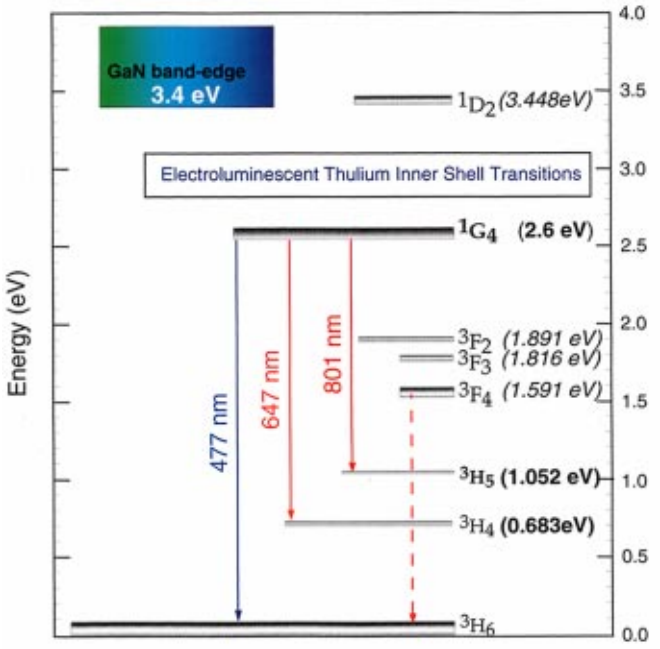

FIG. 3. Energy levels and electroluminescent transitions in Tm-doped GaN.

than that of the near-IR peak. Photoluminescence (PL) characterization of the same GaN:Tm films grown on Si performed with a He–Cd laser excitation source at a wavelength of 325 nm, corresponding to an energy greater than the GaN band gap, also produced emission from the same two Tm transitions.

The emission lines observed from the operation of the GaN:Tm ELD have been identified as transitions between Tm *4f* inner shell levels. Figure 3 indicates the relevant Tm levels contained within the GaN band gap. The energy value in parentheses next to each level is obtained from either reported values[17] for Tm^{3+} in Y_2O_3 (shown in italics) or calculated from our EL spectrum (shown in bold). The blue emission at 477 nm is caused by electronic transition from the $^1G_4$ level to the $^3H_6$ ground state of Tm. The near-IR line at 801 nm can be associated with either the transition between the $^3F_4$ and $^3H_6$ levels or between the $^1G_4$ and $^3H_5$ levels. We attribute the smaller red peak at 647 nm to the transition between the $^1G_4$ and $^3H_4$ levels. It should be

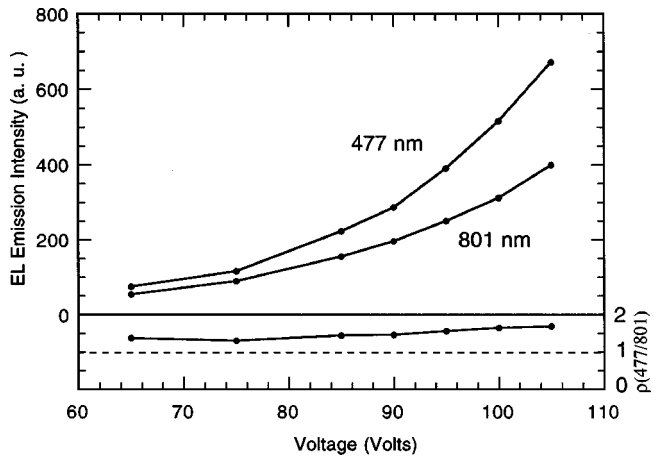

FIG. 4. EL of 477 and 802 nm lines (and their ratio) as a function of applied voltage.

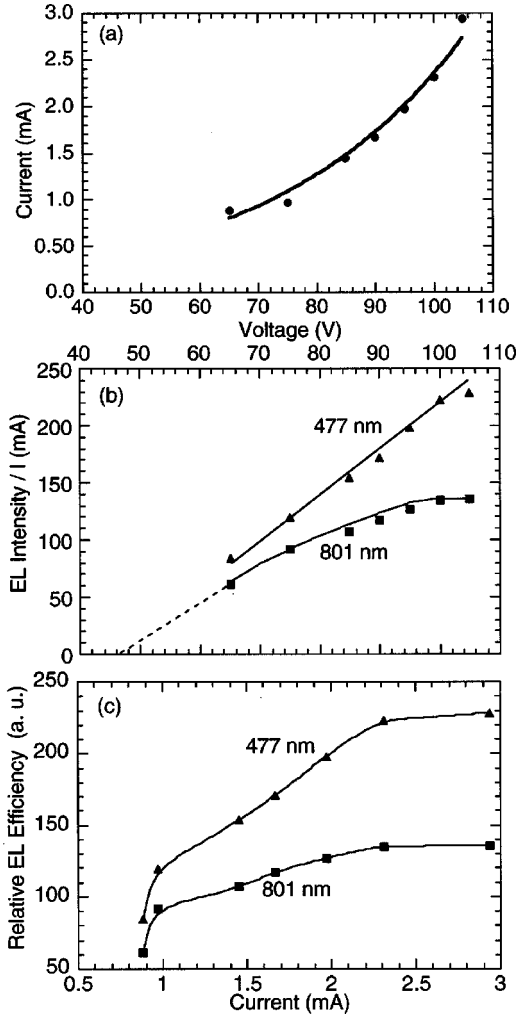

FIG. 5. Relationship between EL intensity, current, and voltage: (a) ELD current–voltage characteristic; (b) and (c) EL emission relative efficiency (intensity normalized by ELD current) as a function of voltage and current.

pointed out that the energy assignment reported in the literature for the $^3F_4$ and $^3H_4$ levels in Tm is frequently reversed. The minor peaks seen in Fig. 3 at 533 and 701 nm have not yet been unambiguously assigned.

The EL emission intensity of the 477 and 801 nm lines are shown in Fig. 4 as a function of applied voltage. The ratio of the blue to IR emission intensities ($\rho_{488/801}$)also plotted in Fig. 4 shows only a slight increase (~23%) with voltage, from 1.37 at 65 V to 1.68 at 105 V. This behavior of $\rho_{488/801}$ in GaN:Tm is similar to that reported[18] in ZnO:Tm with In–Ga electrodes, where $\rho_{488/801}$ increases by only ~14% over a fivefold increase in applied voltage. In contrast, in the case reported[11] for ZnO:Tm in contact with aqueous electrolytic solutions, $\rho_{488/801}$ increases tenfold with an increase in applied potential of a factor of two. The effective voltage independence of $\rho_{488/801}$ indicates that the same excitation mechanism is responsible for the luminescence of both peaks. Therefore, this points to the 801 nm emission originating from the $^1G_4$ level, as does the 477 nm emission.

The relationship between electroluminescence, current, and voltage of the GaN:Tm ELD is shown in several graphs of Fig. 5 for a single device. The *I–V* characteristic of Fig. 5(a) indicates a weak exponential power dependence which can be fit to the equation $I=Ae^{V/V_0}$, where V_0 is approximately 28 V. The EL relative efficiency, defined as the EL intensity divided by the bias current, is shown as a function of device voltage and current in Figs. 5(b) and 5(c), respectively. The relative EL efficiency for both 477 and 801 nm emissions shows a sharp threshold at ~0.8 mA, followed by a region of linear increase. It is interesting to point out in the linear regime, the slope of the 477 nm line is roughly twice that of the 801 nm line. For bias currents larger than ~2.3 mA, the efficiency is essentially constant. The voltage dependence of the relative EL efficiency shows a different behavior for the emission lines. As seen in Fig. 5(b), the relative EL efficiency at 477 nm increases linearly with voltage, while for the 801 nm a pronounced saturation is observed. However, both curves extrapolate to approximately the same threshold voltage of ~46 V. In the future it is important to determine the absolute efficiency values for the different various wavelengths emitted by the GaN:Tm ELD. The relative EL efficiency data presented here represents only a preliminary trend.

In summary, we have reported the blue emission and the electroluminescence characteristics of Tm-doped GaN. In conjunction with our previous results with green emission from GaN:Er and red emission from GaN:Pr, we have now shown that the entire visible spectrum can be covered by utilizing GaN devices doped with various rare earths.

This work was supported in part by a BMDO/ARO contract and an ARO AASERT grant. Equipment support was provided by an ARO URI grant and the Ohio Materials Network.

[1] For a review of LEDs see *High Brightness Light Emitting Diodes*, G. B. Stringfellow and M. G. Craford, volume editors; *Semiconductors and Semimetals*, R. K. Willardson and E. R. Weber, series editors (Academic, New York, 1997), Vol. 48.
[2] I. Akasaki and H. Amano, Ref. 1, Chap. 7.
[3] S. Nakamura, Ref. 1, Chap. 8.
[4] A. J. Steckl and R. Birkhahn, Appl. Phys. Lett. **73**, 1700 (1998).
[5] R. Birkhahn and A. J. Steckl, Appl. Phys. Lett. **73**, 2143 (1998).
[6] A. J. Steckl, M. Garter, R. Birkhahn, and J. D. Scofield, Appl. Phys. Lett. **73**, 2450 (1998).
[7] M. Garter, J. Scofield, R. Birkhahn, and A. J. Steckl, Appl. Phys. Lett. **74**, 182 (1999).
[8] R. Birkhahn, M. Garter, and A. J. Steckl, Appl. Phys. Lett. **74**, 2161 (1999).
[9] M. Garter, R. Birkhahn, A. J. Steckl, and J. D. Scofield, MRS Internet J. Nitride Semicond. Res. **4S1**, G11.3 (1999).
[10] R. E. Shrader, S. Larach, and P. N. Yocom, J. Appl. Phys. **42**, 4529 (1971).
[11] S. Bachir, J. C. Ronfard-Haret, K. Azuma, D. Kouyate, and J. Kossanyi, Chem. Phys. Lett. **213**, 54 (1993).
[12] L. Esterowitz, Opt. Eng. (Bellingham) **29**, 676 (1990).
[13] J. Y. Allain, M. Monerie, and H. Poignant, Electron. Lett. **26**, 166 (1990).
[14] E. Rukmini and C. K. Jayasankar, J. Non-Cryst. Solids **176**, 213 (1994).
[15] G. Ozen, A. Kermaoui, J. P. Denis, X. Wu, F. Pelle, and B. Blanzat, J. Lumin. **63**, 86 (1995).
[16] H. Lozykowski, W. M. Jadwisienczack, and I. M. Brown, Appl. Phys. Lett. **74**, 1129 (1999).
[17] G. H. Dieke, in *Spectra and Energy Levels of Rare Earth Ions in Crystals*, edited by H. M. Crosswhite and H. Crosswhite (Wiley, New York, 1968), pp. 310–312.
[18] S. Bachir, C. Sandouly, J. Kossanyi, and J. C. Ronfard-Haret, J. Phys. Chem. Solids **57**, 1869 (1996).