Selective enhancement of blue electroluminescence from GaN:Tm

D. S. Lee and A. J. Steckl[a)]
Nanoelectronics Laboratory, University of Cincinnati, Cincinnati, Ohio 45221-0030

(Received 10 September 2002; accepted 7 November 2002)

Selective enhancement of electroluminescent emission from high-energy transitions in Tm-doped GaN has been observed to be a strong function of GaN growth temperature. GaN:Tm thin films have been grown by molecular beam epitaxy at temperatures from 100 to 700 °C. At low growth temperatures (100–200 °C) the low energy (infrared-801 nm) transition dominates, while at higher growth temperatures (400–700 °C) the high energy (blue-477 nm) transition dominates. For films grown at low temperatures the main emission excitation mechanism is impact excitation, while for films grown at higher temperatures (≥600 °C) the main excitation mechanism appears to be lattice impact ionization followed by energy transfer to Tm ions. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1534414]

The primary challenge of rare-earth (RE) based electroluminescent (EL) devices remains the development of bright and efficient blue emission.[1,2] Historically, ZnS:Tm has been one of the main candidates for a blue EL emitter since it has long been known for its high efficiency in photoluminescence (PL) and cathodoluminescence[3,4] (CL). Unfortunately, until now emission from Tm-doped thin film EL (TFEL) devices has been dominated by near-infrared (IR) emission (at 800 nm) with only relatively weak blue emission (at 480 nm) from Tm-doped II–VI hosts including ZnS,[5–9] SrS,[10] CaS,[11] and ZnO.[12,13] The two characteristic emissions are caused by $4f-4f$ inner shell transitions of Tm^{3+} ions: the blue emission from the transition, $^1G_4 \rightarrow {}^3H_6$; the IR emission, $^3F_4 \rightarrow {}^3H_6$. A very important analysis of Tm excitation mechanisms in ZnS has been reported[6] by Tanaka *et al.* They have found that in PL spectra from ZnS:Tm blue emission is larger than IR, whereas in TFEL devices the IR emission is strongly dominant. They attributed the PL emission mechanism to photoionization of the ZnS host followed by nonradiative transfer to Tm centers and then by radiative Tm inner shell transitions. By contrast, in EL excitation they ascribe the dominance of the IR emission to an inefficient impact lattice ionization being replaced in importance by Tm direct impact excitation by a hot electron distribution which has dissipated much of its energy through scattering from the low-lying energy levels (^3H and ^3F) of Tm ions. Interestingly, powder-based ZnS:Tm EL with dominant blue emission has been reported[14] by Stambouli *et al.* Since the powder is formed at high temperature (1000–1500 °C), the ZnS:Tm grains are probably sufficiently large and crystalline to enable efficient lattice impact ionization. Unfortunately, the powder EL devices which they report also have a relatively low brightness and high threshold voltage. We have investigated the wide band-gap III–V semiconductor GaN as a host for TFEL devices, previously reporting[15] dominant blue EL emission from GaN:Tm. In this article we report on the critical effect of growth temperature on blue emission and its intensity ratio to infrared emission.

GaN films were grown on *p*-type (111) Si substrates by molecular beam epitaxy (MBE) with a Ga elemental source and a nitrogen plasma source. Doping was performed *in situ* during growth from a solid Tm source. GaN:Tm layers were typically grown for 1 h with a growth rate of 0.5–1.0 μm/h. Ring-shaped Schottky diodes were fabricated for EL measurements using indium–tin–oxide (ITO) sputtering and a liftoff process. The fabrication and operation of these rare-earth-doped GaN (GaN:RE) EL devices has been previously reported.[16]

Tm-doped GaN films were grown at various temperatures from 100 to 700 °C. These temperatures were measured with a thermocouple mounted behind the sample holder. The GaN:Tm growth was performed under slightly N-rich growth conditions: 1.5 sccm for nitrogen flow rate and 400 W for plasma power. Though it is well accepted that good quality crystalline GaN is usually grown under slightly Ga-rich growth conditions,[17] we have previously shown[18] that slightly N-rich growth conditions are favorable for GaN:RE EL emission and the resulting films usually have columnar structure.

Figure 1 compares the blue emission from GaN:Tm EL devices on films grown at different growth temperatures with the structure and morphology of those films. Figures 1(a)–1(c) correspond to the blue emission at −40 V dc bias from EL devices on films grown at 100, 300, and 600 °C, respectively. One can clearly see that the EL emission becomes brighter as the growth temperature increases. This effect is not due simply to changes in film conductivity, as the weakest emission (the 100 °C film) occurred at the highest current: current flow during the emission was 115, 14, and 56 mA, respectively.

SEM images are shown in Figs. 1(d)–1(f) for the films grown at 100, 300, and 600 °C, respectively. The GaN grain size increases with growth temperature from ~30 to 40 nm at 100 °C to ~100 nm at 600 °C. At the same time, the grain shape evolves from sharp needles to rather round-edged pillars. The EL brightness and intensity ratio of blue emission (at 477 nm) to infrared (at 801 nm) are strongly related to grain size, as shown below.

a)Electronic mail: a.steckl@uc.edu

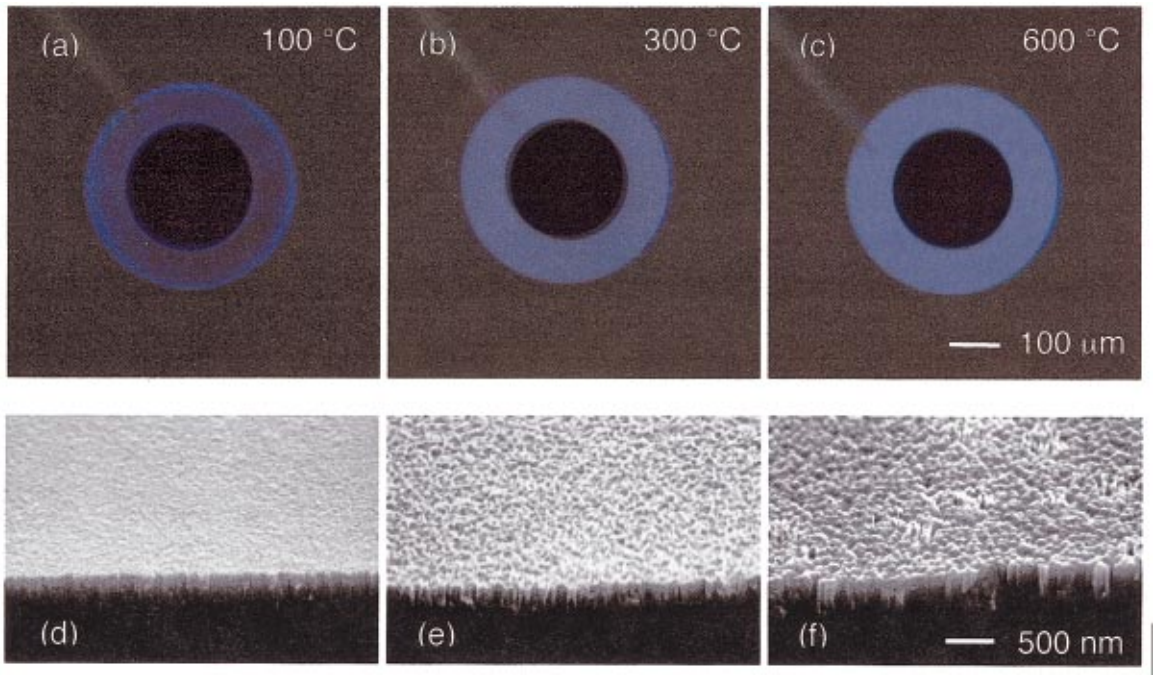

FIG. 1. (Color) Blue EL emission from GaN:Tm ELDs on films grown at several temperatures: (a) 100 °C; (b) 300 °C; (c) 600 °C. SEM images of corresponding films grown at: (d) 100 °C; (e) 300 °C; (f) 600 °C. Bias conditions of −40 V and current of: (a) 115 mA; (b) 14 mA; (c) 56 mA.

The three EL spectra given in Fig. 2 were measured from films grown at 100, 300, and 500 °C. The blue (477 nm) and red (647 nm) levels are caused by transitions from the same excited level ($^1G_4$). The IR (801 nm) level is given by radiative relaxation from a different excited level ($^3F_4$). We can see that the blue emission is involved with high energy transition, while infrared emission is with low energy transition. We can also see very clearly that not only do the blue and IR peaks increase with growth temperature, but that the ratio of the 477 nm emission to the 801 nm one increases as well.

In order to better understand the behavior of these emission levels with growth temperature, in Fig. 3(a) we plot the ratio of blue to infrared EL intensity, denoted as ρ_1, and the ratio of blue EL intensity to the weak red peak, denoted as ρ_2, versus growth temperature. While ρ_2 is nearly constant over the temperature range, ρ_1 appears as a strong function of growth temperature. The data plotted in Fig. 3(a) are based on the ratios of peak intensities. Using integrated intensity centered on each emission line gives the same basic trends. The temperature independence of ρ_2 supports the assumption that both 477 and 647 nm emissions originate from the same excited Tm^{3+} state. The growth temperature dependence of ρ_1 is probably linked to concomitant effects on the GaN grain size, shown in Fig. 3(b). A larger grain size due to higher growth temperature enables a higher average energy of hot electrons for impact excitation, which in turn results in increased probability for the higher energy level transitions.

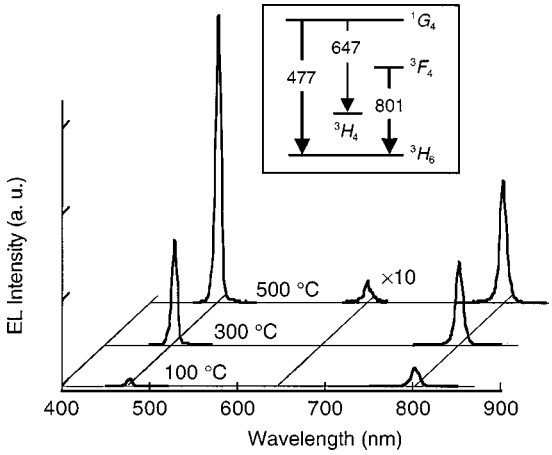

FIG. 2. EL spectra from GaN:Tm films grown at 100, 300, and 500 °C. Three characteristic peaks are monitored at 477 nm (blue), 647 nm, and 801 nm (infrared). Inset shows corresponding $4f-4f$ inner shell transitions in Tm^{3+} ions. Note that the intensity of the 477 nm peak relative to the 801 nm peak increases with growth temperature.

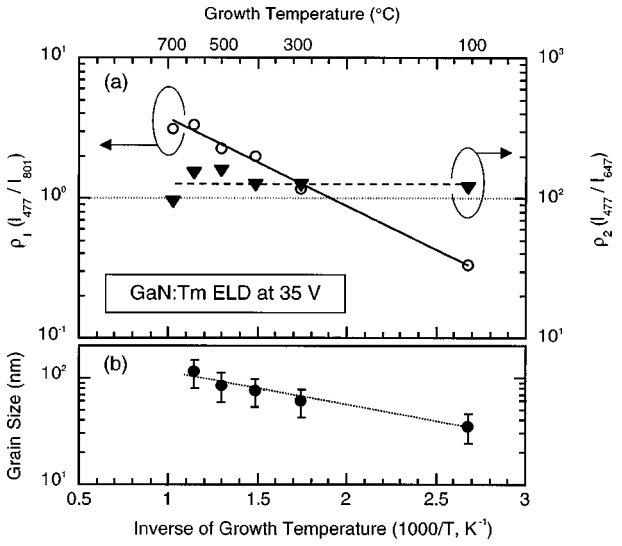

FIG. 3. Growth temperature dependence of (a) intensity ratio of 477–801 nm peaks, ρ_1, and intensity ratio of 477–647 nm peaks, ρ_2. Note, that ρ_1 increases with growth temperature, while ρ_2 stays nearly constant, (b) GaN grain size.

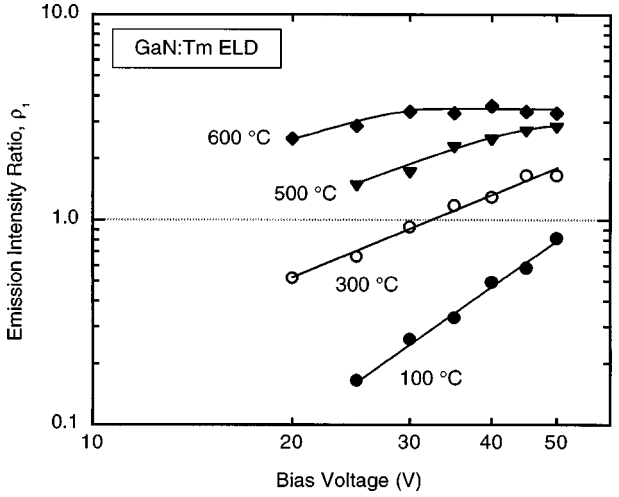

FIG. 4. Intensity ratio of 477–801 nm peaks (ρ_1) vs bias voltage. Note that ρ_1 monotonically increases with the growth temperature and that values of $\rho_1 > 1$ (i.e., blue dominant emission) are obtained. Power law dependence of ρ_1 on bias voltage indicates that the dominant excitation mechanism is direct impact excitation of Tm ions by hot electrons. Constant value of ρ_1 with bias voltage is likely caused by impact ionization of the GaN host followed by energy transfer to Tm ions.

Interestingly, ρ_1 shows an Arrhenius-like behavior with an activation energy of 0.122 eV, while the grain size activation energy with growth temperature is 0.062 eV.

The XRD intensity and full width at half-maximum (FWHM) of the (0002) peak from hexagonal GaN exhibit a complementary dependence on growth temperature (not shown here) as previously reported[19] for GaN:Er films, namely that crystallinity improves with growth temperature up to ~500 °C and then seems to remain more or less constant for higher temperatures.

Figure 4 shows the emission intensity ratio ρ_1 as a function of bias voltage of EL devices for films grown at various temperatures. For films grown at lower temperatures (100–300 °C) ρ_1 increases with a power law dependence ($\rho_1 \sim V^n$) on bias (the relationship is linear in this log–log plot). As the GaN:Tm film growth temperature increases, a weaker dependence of emission intensity on bias is observed (i.e., n decreases). Furthermore, for the films grown at higher temperature ($\geqslant$500 °C), a saturation effect is observed at larger bias values. The power law dependence of ρ_1 with bias has been attributed[11,20] to direct impact excitation of luminescent centers as the dominant mechanism. The case of constant ρ_1 with bias is attributed[11] to the two-step excitation process consisting of impact ionization of the host followed by energy transfer to luminescent centers. Impact ionization is known[6] to be a much more efficient mechanism to excite Tm ions to the $^1G_4$ level than impact excitation. It appears that for films grown at low temperatures the dominant mechanism for blue emission as well as IR emission is direct Tm impact excitation. As the growth temperature increases, a gradual shift to impact ionization of GaN followed by energy transfer to Tm ions is observed.

In summary, EL emission from GaN:Tm was investigated for EL devices on films grown at various temperatures, from 100 to 700 °C. The intensity ratio of emission by high-energy transition (blue −477 nm) to emission by low-energy transition (infrared −801 nm) increases monotonically with growth temperature reaching a value of $\geqslant$3. This is the result of better crystallinity (equivalently, larger grain size) of the film at high temperature. EL devices fabricated on films grown at higher temperature have a constant blue/infrared intensity ratio, indicating that the dominant excitation mechanism is impact ionization of GaN followed by energy transfer to Tm ions. Obtaining blue dominant emission ($\rho_1 > 1$) from Tm ions indicates GaN is an excellent host material choice. Strong blue emission from GaN:Tm EL devices, in combination with green emission from GaN:Er and red emission from GaN:Eu indicates that full-color displays can be obtained with the single host, GaN.

This work was supported by ARO and ARL Grants. The authors are pleased to acknowledge the support of D. Morton and J. Zavada.

[1] G. Härkönen, M. Leppänen, E. Soininen, R. Törnqvist, and J. Viljanen, J. Alloys Compd. **225**, 552 (1995).
[2] C. N. King, J. Vac. Sci. Technol. A **14**, 1729 (1996).
[3] S. Ibhku and D. W. Langer, Appl. Phys. Lett. **2**, 95 (1963).
[4] R. E. Shrader, S. Larach, and P. N. Yocom, J. Appl. Phys. **42**, 4529 (1971).
[5] H. Kobayashi, S. Tanaka, V. Shanker, M. Shiiki, T. Kunou, J. Mita, and H. Sasakura, Phys. Status Solidi A **88**, 713 (1985).
[6] S. Tanaka, S. Morimoto, K. Yamada, H. Kobayashi, Z. Zhang, and X. Jiang, J. Cryst. Growth **117**, 997 (1992).
[7] X. Jiang, Z. Zhang, W. Zhao, Z. Lui, and S. Xu, J. Phys.: Condens. Matter **6**, 3279 (1994).
[8] A. B. Stambouli, S. Hamzaoui, and M. Bouderbala, Thin Solid Films **283**, 204 (1996).
[9] S. H. Sohn, D. G. Hyun, A. Yamada, and Y. Hamakawa, Appl. Phys. Lett. **62**, 991 (1993).
[10] P. D. Keir, C. Maddix, B. A. Baukol, J. F. Wager, B. L. Clark, and D. A. Keszler, J. Appl. Phys. **86**, 6810 (1999).
[11] J. M. Sun, G. Z. Zhong, X. W. Fan, C. W. Zheng, G. O. Mueller, and R. Mueller-Mach, J. Appl. Phys. **83**, 3374 (1998).
[12] S. Bachir, C. Sandouly, J. Kossanyi, and J. C. Ronfard-Haret, J. Phys. Chem. Solids **57**, 1869 (1996).
[13] J. C. Ronfard-Haret and J. Kossanyi, Chem. Phys. **241**, 339 (1999).
[14] A. B. Stambouli, S. Hamzaoui, M. Bouderbala, and O. K. Omar, Appl. Energy **64**, 207 (1999).
[15] A. J. Steckl, M. Garter, D. S. Lee, J. Heikenfeld, and R. Birkhahn, Appl. Phys. Lett. **75**, 2184 (1999).
[16] M. J. Garter and A. J. Steckl, IEEE Trans. Electron Devices **49**, 48 (2002).
[17] E. Calleja, M. A. Sanchez-Garcia, F. J. Sanchez, F. Calle, F. B. Naranjo, E. Munoz, U. Jahn, and K. Ploog, Phys. Rev. B **62**, 16826 (2000).
[18] D. S. Lee and A. J. Steckl, Appl. Phys. Lett. **80**, 728 (2002).
[19] D. S. Lee, J. Heikenfeld, and A. J. Steckl, Appl. Phys. Lett. **80**, 344 (2002).
[20] D. C. Krupka, J. Appl. Phys. **43**, 476 (1972).