

# Rare Earth Doped Gallium Nitride — Light Emission from Ultraviolet to Infrared

A. J. STECKL\*, J. HEIKENFELD, M. GARTER, R. BIRKHAHN and D. S. LEE

Nanoelectronics Laboratory

University of Cincinnati

\* E-mail: a.steckl@uc.edu

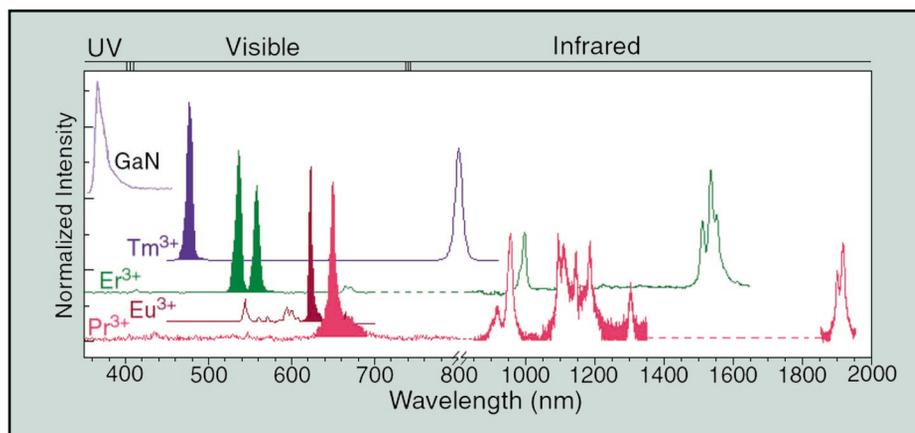
The lanthanide elements, commonly known as the “rare earths” (RE), have been an increasingly important ingredient in a variety of photonic applications [1], ranging from solid-state lasers to color displays to optical fiber telecommunications. RE elements have a partially filled inner ( $4f^n$ ) shell shielded from its surroundings by completely filled outer ( $5s^2$  and  $5p^6$ ) orbitals. This results in optical emission of very sharp lines at wavelengths from the UV to the IR, which are relatively independent of the host material and are determined by the energy of the transition between  $4f$  states of the RE. While the host material has a weak influence on the emission wavelength, it does have a very strong effect on the radiative transition probability. In general, doping of conventional semiconductors (Si, GaAs, etc.) with REs has suffered from limited solubility and severe temperature quenching, which has made the room temperature operation impractical.

## Emission Peaks

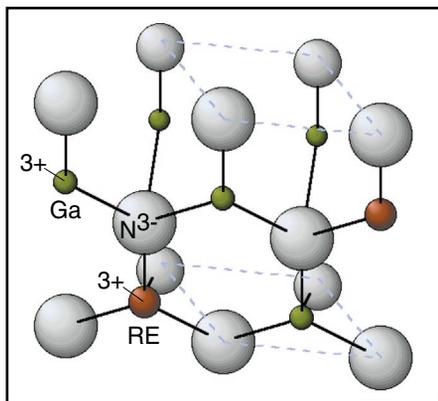
In this paper we briefly review the recent breakthroughs made with the incorporation of trivalent rare earth ( $RE^{3+}$ ) elements into GaN films and resulting light emitting devices. GaN is a wide bandgap semiconductor that is intensely investigated [2] for optical and electronic applications.  $Er^{3+}$  doping of GaN has been shown to produce strong near-IR  $1.5\ \mu\text{m}$  emission suitable for fiber optic telecommunications from the lowest excited state. At Cincinnati, we have obtained for the first time photoemission from higher excited RE states in GaN covering the entire visible spectrum: light emission in the green (from Er at 537/558 nm) [3,4,5], red (Pr at 650 nm, Eu at 621nm) [6,7], and blue (Tm at 477 nm) [8]. Emission in the near-infrared (IR) is also obtained at 801 nm from Tm [8], at 1000 and 1540 nm from Er [5], and at 956, 1303 and 1914 nm from Pr [6].

The rare earths were introduced during growth of the GaN layer by MBE on either sapphire or Si substrates. Figure 1 shows emission spectra from electroluminescent devices (ELD) for GaN doped with Tm, Er, Pr and Eu. Also shown in Figure 1 is the intrinsic GaN emission in the ultraviolet part of the spectrum at  $\sim 365\ \text{nm}$ . The primary visible colors emitted by GaN ELDs doped with these individual REs are very “pure” and match very well the CIE coordinates adopted by the National Television System Committee (NTSC).

In addition to the pure colors, mixed colors have been obtained by co-doping GaN films with a combination of REs. As seen on the cover of this issue and discussed in more detail below, GaN:RE ELDs have been developed which emit in a variety of pure and mixed colors. In general, emission from GaN:RE is surprisingly strong, being observable with the naked eye at room temperature. Significant signal reduction with temperature is generally not observed until well above room temperature. Thus, rare-earth-doping of GaN represents an interesting alternative to semiconductor alloying (GaN/InN/AlN) for visible light emis-



**Figure 1.** The emission spectrum of several different RE-doped GaN films from visible to IR wavelengths. All spectra are normalized to their own highest value and are not readily comparable to each other in intensity. The color of the GaN:Tm emission is blue, GaN:Er is in the green, and both GaN:Eu and GaN:Pr emit in the red. For the visible region, all spectra were taken from working ELDs. In the IR region, the GaN:Tm and the GaN:Er spectra are from working EL devices while the GaN:Pr is from PL data.



**Figure 2. Preliminary model of the GaN:RE crystal structure. The Er-N bond has been measured to be 2.17 Å, versus a Ga-N bond length of 1.95 Å.**

sion applications and has the additional attractive aspect of strong IR emission for telecommunications and other applications. The use of Si as the substrate material for GaN:RE ELDs is another clear advantage of this technology.

## Rare Earth Incorporation

Theoretically, RE intra- $4f^n$  atomic transitions are parity forbidden by the Laporte selection rule. RE ions incorporated into a partially ionic solid frequently substitutionally occupy the cation site. In the cation site an uneven ligand crystal field relaxes the selection rule and increases the probability of intra- $4f^n$  transitions [9]. These  $4f-4f$  transitions, however, are still not fully allowed, resulting in excited state lifetimes of  $\sim 10^{-3}$  s for RE-doped systems. In wurtzitic GaN, which has a significant component of ionic bonding, the  $RE^{3+}$  ions have strong optical activity levels, since they are generally substitutionally located on the Ga sub-lattice where the lack of inversion symmetry produces strong ligand fields thereby increasing the  $4f-4f$  transition probability. These substitutional RE dopants are therefore likely to be the optically active RE centers observed in GaN:RE.

A preliminary model of the GaN:RE crystal structure is shown in Figure 2. A strongly bonded GaN lattice, in conjunction with substitutional incorporation [10] allows unusually high RE doping concentrations (up to at least  $\sim 1$  at. %) with no quenching or saturation of the optical signal. By comparison, the use of

$RE^{3+}$ -doped II-VI semiconductors as emitters and phosphors suffers from a more weakly bonded lattice, and substitutional location of the  $RE^{3+}$  ions on the  $2+$  cation sites, which generates electrically-active defects due to lack of charge neutrality.

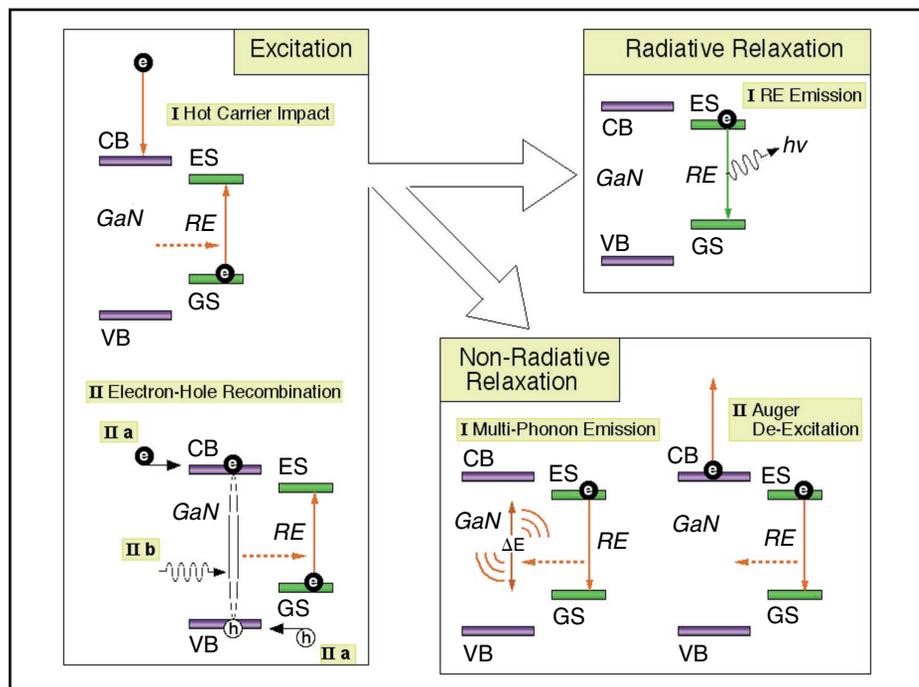
RBS channeling analysis [11] confirms that a great majority ( $\sim 90\%$ ) of the Er ions occupy substitutional sites on the Ga sublattice even at relatively high concentrations of  $>0.1$  at.%. The Er-N bond has been measured by EXAFS analysis [12] to be 2.17 Å, versus a Ga-N bond length of 1.95 Å. This unusually short Er-nearest neighbor bond length in GaN is thought to be due to two major factors: (a) the low 4-fold coordination, compared for example to a 12-fold coordination in  $ErSi_2$ ; (b) a more polar bond for the Er-N than for Ga-N (due to electronegativity differences), which helps to energetically compensate for the Ga - Er size mismatch.

Light emission from GaN:RE has been demonstrated via photoluminescence (PL), cathodoluminescence (CL), and electroluminescence (EL). The dominant mechanisms for excitation and subsequent relaxation of RE dopants in GaN

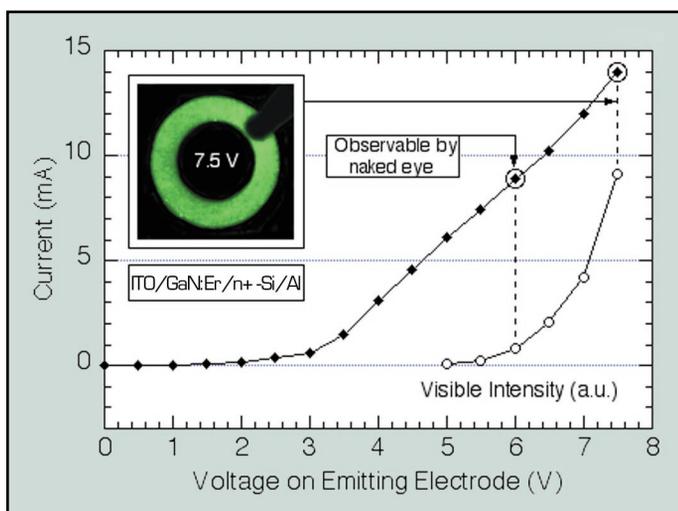
are depicted in Figure 3. In PL electron-hole pairs are generated by above band-gap photon absorption, carrier generation is provided by a high energy electron beam in CL, and in EL carrier injection occurs by the application of bias voltage to electrical contacts on the GaN layer.

## Low Voltage ELD

The form of EL that the GaN:RE ELDs utilize involves impact excitation of RE dopants. In order for hot carrier excitation to occur, a high electric field is applied across the GaN layer. Green light emission from GaN:Er ELDs has been observed at an applied bias as low as 5 V. This indicates that the minimum field strength required for GaN:RE ELDs is an order of magnitude lower than the 1-2 MV/cm required for II-VI:RE based ELDs. In Figure 4, a low voltage GaN:Er ELD is shown emitting green light at a bias of 7.5 V, along with a corresponding graph of current and light intensity vs. applied voltage. The device consists of an Er-doped GaN layer grown by MBE on an  $n^+$  Si substrate and a top-side circular ("ring contact") transparent bias electrode of In-Sn oxide (ITO). The combination of



**Figure 3. The dominant mechanisms for excitation and subsequent relaxation of RE dopants in GaN. Shown schematically in the diagrams are the conduction band (CB) and valence band (VB) edges of GaN and the ground state (GS) and excited state (ES) for RE transitions.**



**Figure 4.** GaN:Er ELD current and EL intensity as a function of voltage on emitting electrode. A thin ( $\sim 300$  nm) GaN layer and  $n^+$  Si substrate are used to obtain low-voltage optical turn-on at 6V. The inset is a photograph of green emission under the ITO bias electrode at 7.5 V.

this very simple device structure with the use of Si substrate indicates the potential of this technology for low-cost displays and for integration with Si technology for drive and control circuitry.

## 1.5 $\mu\text{m}$ Operation

A second major application of RE-doped GaN is in the area of fiber optic telecommunications, which has seen explosive growth in terms of both new network installation and network bandwidth. Fiber optic signals carry near-IR wavelengths, primarily 1.5  $\mu\text{m}$  and secondarily 1.3  $\mu\text{m}$ , which are the wavelengths of minimum loss and minimum dispersion in silica fibers.

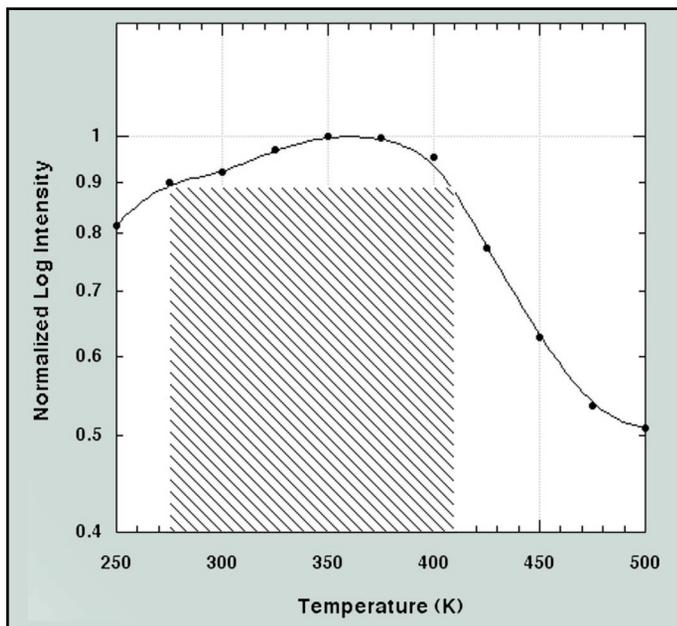
Fiber optic sources and amplifiers have been developed using  $\text{Er}^{3+}$  and  $\text{Pr}^{3+}$  doped in a variety of glasses. Semiconductor-based equivalents that could take advantage of semiconductor technology for miniaturization and operation, have suffered from low solubility and thermal quenching. Extensive research has been carried out on Er-doped Si (for reviews see Coffa et al. [13] and Fitzgerald and Kimmerling [14]). The IR radiation is nearly completely quenched at temperatures around 200 K. The addition of a significant oxygen concentration has also been shown to improve the Er temperature quenching in silicon [15,16] but at the expense of a more complicated process and degraded electrical properties. An increasing semiconductor bandgap has also been shown to reduce temperature quenching [17]. GaP, which has a larger bandgap than Si, still exhibits [18] a reduction in EL intensity at 300 K compared to low temperature values.

In Er-doped GaN, the thermal quenching is for all practical purposes, no longer a problem. Figure 5 shows the temperature

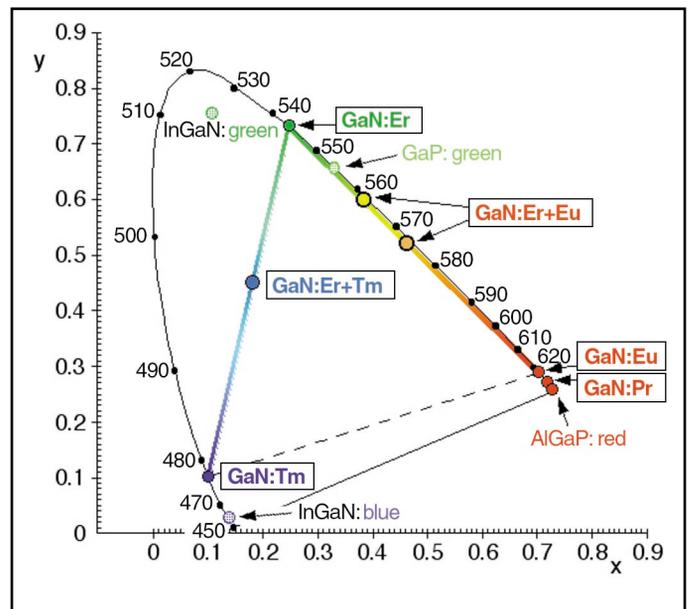
dependence of the 1.5  $\mu\text{m}$  electroluminescence of a GaN:Er ELD. Notice that the EL intensity actually peaks at around 375 K. A practical operating temperature range for these devices would be from 275 K to 410 K, representing a maximum  $\pm 5\%$  deviation in signal intensity. This is important especially when considering the temperature quenching of the IR light emission in other semiconductor hosts. We therefore conclude that GaN has a significant advantage as a host for erbium compared to GaAs, GaP and Si, which have been extensively studied for Er-based light emitting applications. In the case of GaN:Er, it appears that devices could be developed for semiconductor light sources and amplifiers of 1.5  $\mu\text{m}$  signals.

## Pure and Mixed Colors

The versatility of the GaN:RE technology is illustrated using the CIE chromaticity diagram shown in Figure 6. The triangle in the diagram connects the three primary visible colors emitted by the GaN doped with Tm (blue), Er (green), and Eu and Pr (red). The coordinates of this triangle match very well the standard primary colors of the NTSC. In addition to primary colors, mixed colors or hues can be obtained by incorporating multiple REs into the GaN layer, whose combined emission is perceived by the eye as a range of colors depending on the relative intensities of the constituents. Examples of mixed colors shown in Figure 6 are a combination of Er and Tm yielding the cyan color and Er and Eu producing orange and yellow colors. The ability of RE-doped GaN technology to cover the visible color spectrum with both primary and mixed colors makes it a strong candidate for a variety of display and lighting applications.



**Figure 5.** Temperature dependence of the 1.5  $\mu\text{m}$  electroluminescence of a GaN:Er ELD. The shaded region indicates the useful operating temperature range, corresponding to a maximum  $\pm 5\%$  change in signal intensity.



**Figure 6.** CIE  $x$ - $y$  chromaticity diagram showing the location of pure color emission from GaN ELDs doped with Tm (blue), Er (green), Eu (red) and Pr (red) and of mixed color emission using GaN:Er+Tm (cyan) and yellow and orange emission from the GaN:Er+Eu ELD. Also shown are the coordinates of other commercial LEDs.

The authors are pleased to acknowledge the support of this work by BMDO/ARO and the contributions of their many collaborators at other institutions.

## References

- [1] For a review of photonic applications of rare-earth-doped semiconductors and other materials, see A. J. Steckl and J. M. Zavada, *MRS Bulletin* 1999, 24 (9), p. 16, and articles therein.
- [2] For an in-depth and up-to-date treatment of GaN and related alloys, see H. Morkoc, *Nitride Semiconductors and Devices*, Springer 1999 (Berlin).
- [3] A. J. Steckl and R. Birkhahn, *Appl. Phys. Lett.* 1998, 73 (12), p. 1700
- [4] A. J. Steckl et al., *Appl. Phys. Lett.* 1998, 73 (17), p. 2450
- [5] M. Garter et al., *Appl. Phys. Lett.* 1999, 74 (2), p. 182
- [6] R. Birkhahn et al., *Appl. Phys. Lett.* 1999, 74 (15), p. 2161
- [7] J. Heikenfeld et al., *Appl. Phys. Lett.* 1999, 75 (9), p. 1189
- [8] A. J. Steckl et al., *Appl. Phys. Lett.* 1999, 75 (15), p. 2184
- [9] G. Blasse and B. C. Grabmaier, *Luminescent Materials*, Springer 1994, (Berlin).
- [10] R. Birkhahn et al., *J. Vac. Sci. Technol.* 1999, B 17 (3), p. 1195
- [11] K. Lorenz et al., *Nucl. Instr. Meth. Phys. Res. B*, 2000, 161/163, p. 950
- [12] P. H. Citrin et al., to be published
- [13] S. Coffa et al., *MRS Bulletin*, 1998, 23 (4), p. 25
- [14] E. Fitzgerald and L. Kimmerling, *MRS Bulletin*, 1998, 23 (4), p. 39
- [15] A. Reittinger et al., *Appl. Phys. Lett.* 1999, 70, p. 2431
- [16] J. Stimmer et al., *Appl. Phys. Lett.* 1996, 68, p. 3290
- [17] P. N. Favenec et al., *Electron. Lett.* 1989, 25, p. 718
- [18] G. M. Ford and B. W. Wessels, *Appl. Phys. Lett.* 1996, 68, p. 1126