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Multiple color capability from rare earth-doped gallium nitride

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Abstract

Rare earth (RE) doping of GaN has led to a new full color thin film electroluminescent (TFEL) phosphor system. GaN films doped with Eu, Er, and Tm dopants emit pure red, green, and blue emission colors, respectively. As a host for RE luminescent centers, GaN possesses many properties which are ideal for bright multiple color TFEL. Specifically, GaN has excellent high field transport characteristics, is chemically and thermally rugged, and incorporates well the RE dopants. X-ray absorption measurements have shown that even at RE dopant levels exceeding 0.1 at.% the majority of RE dopants occupy a strongly bonded substitutional site on the Ga sublattice. According to RE crystal field theory this tetrahedrally bonded site allows optical activation and emission from RE $4f$–$4f$ inner-shell electronic transitions. Monte Carlo calculations of GaN carrier transport have shown that at ~ 2 MV cm^{-1} applied field the average electron possesses 2.6 eV energy which is adequate for exciting blue emission. GaN:Er TFEL devices have exhibited a brightness of 500–1000 cd/m^2 at ~ 540 nm. In addition to pure colors, mixed colors can be achieved by doping with a combination of REs. For example, co-doping with Er and Tm results in an emission spectrum which is perceived by the human eye as a blue–green (turquoise) hue. Multiple color capability in a single device has also been demonstrated by adjusting the bias voltage (in a co-doped GaN:Er,Eu layer) or by switching the bias polarity (in a stacked two layer GaN:Er/GaN:Eu structure). The combination of pure or mixed color emission, the availability of bias controlled color, and the potential for white light emission indicate that GaN:RE TFEL devices have enormous potential for display applications. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: GaN; Erbium; Thulium; Europium; Thin film electroluminescence

1. Introduction

Recent success with red, green, and blue (RGB) emission from rare earths (REs) in-situ doped [1] during growth or implanted [2] into films of the III–V semiconductor GaN naturally extends itself to the pursuit of multiple color and full color (white) light sources.

Multiple color capability is a primary requirement for flat panel displays (FPDs). Multi-color FPDs utilize either additive generation of light from pure colors or subtractive generation of pure colors from broad spectrum light (backlit liquid crystal displays). Full color capability further requires either well saturated RGB colors or white mixed light. With progress in RGB integration, GaN:RE phosphors can be utilized in either the additive and subtractive formats for multi- and full-color FPDs. Thin film electroluminescence (TFEL) [3] of phosphors based on II–VI semiconductors have already laid claim to FPD applications calling for extreme ruggedness and reliability. TFEL companies are rapidly progressing [4,5] in their quest to capture even larger markets, such as portable displays and flat-TVs. As discussed below, the III–V semiconductor GaN possesses many properties ideal for TFEL, calling for continued development of the GaN:RE phosphor system. Further GaN:RE development has the clear goal of realizing high brightness, superior durability and color capability, in order to advance its commercial applicability.

We report here on advances in GaN:RE phosphor technology, specifically in realizing various forms of multiple color capability from GaN:RE TFEL devices (ELDs). A brief review of the GaN host properties allowing bright, multiple color capability is also included. GaN incorporates very well RE dopants and can provide hot carriers with average energies corresponding to excitation of blue emission. For the GaN:RE material system the possibility of multiple

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color indicators which change color based solely on the polarity or magnitude of applied bias is also of interest. We review results on voltage controlled-(VC)-ELDs [6] and present new results on switchable color (SC)-ELDs [7]. The VC-ELDs progress from red to green emission with increasing bias voltage whereas the SC-ELDs switch from red to green emission based on the polarity of applied bias. Normalized red (Eu), green (Er), and blue (Tm) emission spectrums of individual GaN:RE ELDs are shown in Fig. 1. Also shown is the ~1550 nm emission from GaN:Er which is of particular interest in telecommunications applications [8].

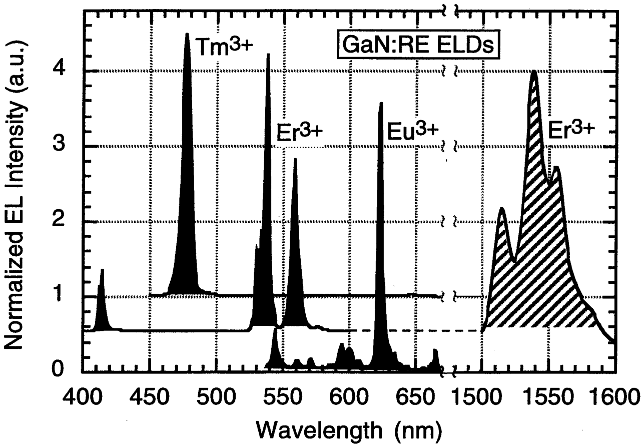
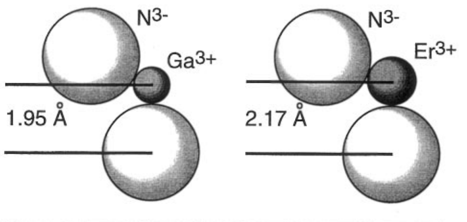


Fig. 1. The emission spectra of Tm, Er, and Eu-doped GaN ELDs showing the visible and IR wavelengths of interest. All spectra are self-normalized and are not readily comparable to each other. The visible peaks for each RE correspond to saturated RGB colors which can be utilized for single-, multiple-, mixed-, and full-color applications. The ~1550 nm emission from GaN:Er is of particular interest in telecommunications applications.



Effective Cation Mismatch

Ga^{3+} 0.47	N^{3-} 1.44	Er^{3+} 0.78	(CN=4)
Si 1.18		Er^{3+} 1.76	(CN=10)
Zn^{2+} 0.60	S^{2-} no data	Er^{3+} 0.78	(CN=4)
Sr^{2+} 1.18	S^{2-} 1.84	Er^{3+} 0.89	(CN=6)
Al^{3+} 0.39	N^{3-} 1.44	Er^{3+} 0.78	(CN=4)

Fig. 2. Drawing (top) indicating experimental data for the Ga–N and Er–N bond length and atomic radii in wurtzite GaN:Er. Table (bottom) of effective ionic radii and coordination number (CN) for Er doped GaN, Si, ZnS, SrS, and AlN.

2. Material system

The RE-doped GaN is grown in a Riber MBE-32 system on 2 in. p-Si (111) substrates. Ga and RE solid sources were used in conjunction with a RF plasma source supplying atomic nitrogen. For GaN:RE ELD operation indium-tin-oxide (ITO) ring contacts were fabricated on the GaN:RE layer. Low voltage [9] GaN:Er ELDs have demonstrated green emission at 5 V DC bias. High brightness GaN:Er ELDs biased with 50–100 V have exhibited a brightness as high as 500–1000 cd/m^2. The intense light emission from GaN:RE ELDs can be partially attributed to the ability of GaN to incorporate large concentrations of optically active RE species. In other semiconductor hosts (such as Si, GaAs), high RE concentrations result in quenching of the emission due to degradation of the host material and or RE precipitation. This ability to incorporate large RE concentrations in GaN is surprising when considering the size mismatch between RE ions and the Ga^{3+} cation, which is larger than in II–VI hosts. For comparison some relevant effective ionic radii [10,11] are listed for Er-doped GaN, Si, ZnS, SrS, and AlN in the table at the right of Fig. 2. An X-ray absorption study [12] of GaN:Er reveals that even at high Er concentrations (>0.1 at.%) the majority of Er ions sit substitutionally on the Ga sublattice. The experimental data for the Ga–N and Er–N bond lengths are reflected in the drawing at the left of Fig. 2. In this Ga substitutional site the tetrahedral bonding about the RE lacks inversion symmetry and results in allowance of normally forbidden RE intrashell $4f$–$4f$ transitions which in turn result visible light emission. GaN can incorporate RE atoms at concentration levels comparable to or greater than that possible with commercial II–VI hosts. This is partially due to the strong bonding nature of GaN (partially covalent) compared with the more weakly bonded II–VI compounds (largely ionic). The experimentally measured Er–N bond length of 2.17 Å is very short, a testament to its bond strength. GaN also possesses the ability to incorporate the trivalent RE ions without violating charge neutrality. Incorporating RE^{3+} in II–VI phosphors such as ZnS:Tb requires co-doping with F or O in order to satisfy charge neutrality and to achieve the best luminance and efficiency values. The brightest GaN:RE ELDs utilize RE dopant levels of 0.1–1% confirming that GaN is an excellent host for allowing large concentrations of RE dopants without severe quenching of light emission. The bonding for all RE elements is roughly similar since they all share an identical outer shell ($5s^25p^6$). This enables straight forward multiple color capability through co-doping GaN with several RE species. The well studied RE $4f$–$4f$ transitions provide several choices of RE dopant in GaN in order to create red (Eu, Pr, Sm), green (Er, Tb), blue (Tm) light and potentially white (Ho, multiple RE's) light.

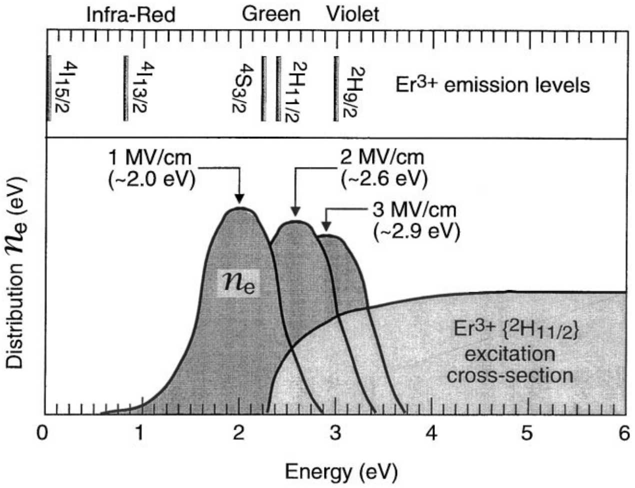


Fig. 3. Qualitative plot of electron energy distribution for 1, 2, and 3 MV cm^{-1} applied field to GaN. The pictured electron distributions are estimated based on average energy only, as determined [13] from Monte Carlo calculations of high field transport in GaN. Also shown is an approximate curve for the Er impact excitation cross-section of the $^2H_{11/2}$ which results in green (~ 2.3 eV) emission. The corresponding energy levels of dominant emissions from Er^{3+} are also shown at the top of the plot.

3. Hot carrier generation

TFEL hosts such as GaN distinguish themselves from phosphors utilized in CL or PL based light emission by their high field electronic transport mechanisms. TFEL hosts need to be able to provide hot carriers with greater than 2 eV energy at an applied field of 1–2 MVcm^{-1}. This requirement has limited efficient TFEL hosts to wide band gap semiconductors. Fig. 3 shows a qualitative plot of electron energy distribution in GaN at several applied field strengths. The pictured electron distributions are presented accurately in average energy only, as taken from Monte Carlo calculations [13] of high field transport in GaN. The calculations show that at ~ 2 MV cm^{-1} applied field the average carrier energy is equal to that required for exciting blue (2.6 eV) emission. Also plotted in Fig. 3 is an approximate curve for the Er impact excitation cross-section of the $^2H_{11/2}$ level which results in green (~ 2.3 eV) emission. If full color capability is to be achieved in a single host, carrier energies nearing 3 eV are required. Currently, the TFEL host SrS, a II–VI compound, most efficiently provides hot carrier excitation with sufficient energy for blue emission. SrS:Cu, Ag and SrS:Ce are excellent blue and blue–green emitters but there does not exist [14] a bright red SrS-based TFEL phosphor in order to realize full color capability in a single host. GaN:RE could potentially provide an efficient full-color phosphor based on a single host.

Carrier transport mechanisms for field strengths on the order of $\sim$MV cm^{-1} are not fully understood at the theoretical level. Although, experimental data can be utilized to provide insight into high field transport behavior. A lanthanide (RE) doping study [15] comparing ZnS and SrS hosts indicates that SrS is a superior material for blue TFEL. In that study the distribution of high energy carriers is obtained approximately by examining the existence and/or strength of blue and violet emission peaks compared with lower energy green, red and IR peaks. We have applied this approach to the evaluation of GaN:Er and GaN:Tm ELDs. The GaN:Er spectrum in Fig. 1 is taken at ~ 1.5 MV cm^{-1} applied field and exhibits a strong emission peak in the violet spectrum (415 nm). Referring to Fig. 3, this 415 nm peak represents a photon energy of ~ 3 eV corresponding to the $^2H_{9/2}$ Er level. This brings the qualitative plots of electron energy distribution into agreement with the observed GaN:Er spectra. For II–VI hosts the ZnS:Er spectrum saturates in the green, whereas SrS:Er has very strong violet peaks. Unlike the case of ZnS:Tm where most of the light emitted is in the IR, GaN:Tm ELDs [16] emit a 477 nm blue emission twice as strong as the emission at 801 nm. Phosphor crystallinity can also play a major role in high field transport. For vertically biased GaN:RE ELDs fabricated with a conductive substrate as the bottom electrode, the tendency of growth in vertical columns is advantageous for high field transport since the number of grain boundaries hot carriers intercept is reduced. In summary, GaN provides adequate hot carrier distributions for excitation of multiple color RE light emission spanning the entire visible spectrum.

4. Tunable and switchable-color ELDs

Given the ability of GaN:RE phosphors to emit light at multiple wavelengths some novel devices can be considered which allow bias control of the emitted color. One such TFEL device structure [17] utilizes stacked individual color ELDs. For this style of multiple color stacked device, the ability to independently drive two distinct light emitters (such as red and green) normally requires three electrical contacts. We have developed GaN:RE ELDs which can emit multiple colors by varying only the electrical bias on two electrodes. The first approach is based on a single GaN film co-doped with Eu and Er. The VC-ELD structure is shown in Fig. 4b. During operation, the emission from VC-ELDs can be adjusted [6] from orange light emission (primarily Eu red, Fig. 4b) to yellow emission (combination of Eu and Er green, Fig. 4a) by merely increasing the applied voltage from -70 to -100 V. The progression from orange to yellow color is likely attributed to differences in impact excitation cross-section parameters. Red emission from Eu with a long excited state lifetime ($^5D_0$–$^7F_2$, ~ 1 ms) should saturate

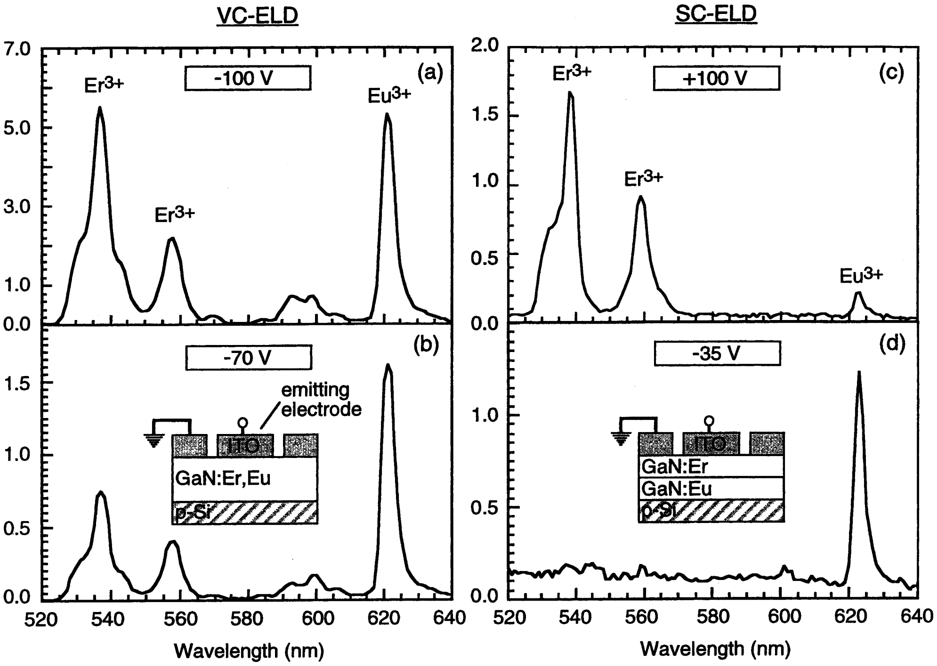


Fig. 4. (a, b) EL intensity measured from an ITO/GaN:Er,Eu/p-Si VC-ELD for − 70 V (orange) and − 100 V (yellow) bias applied to the emitting electrode. (c, d) EL intensity measured from ITO/GaN:Er/GaN:Eu/p-Si SC-ELD for + 100 V positive (green) and − 35 V negative (red) bias applied to the emitting electrode.

with increasing bias current before Er green emission with its shorter lifetime ($^2H_{11/2}$–$^4I_{15/2}$, ~ 0.01 ms). Also, green emission (~ 2.3 eV) requires hotter carriers (higher applied voltage) than red emission (~ 2.1 eV). Other effects such as temperature quenching could also give rise to the voltage control of emission color.

SC-ELDs [7] have also been developed utilizing the GaN:Er/GaN:Eu stacked phosphor structure shown Fig. 4d. The SC-ELDs switch from red to green emission by changing the polarity of the applied voltage: positive bias (+ 100 V, 0.45 mA) for saturated green emission and negative bias (− 35 V, − 2.5 mA) for red. Some of the same underlying effects attributed to color change in VC-ELDs also likely play a role in the SC-ELDs. However, the dominant influence on color switching in SC-ELDs is attributed to polarity dependent current paths through the stacked phosphor layers. In comparison to VC-ELDs the SC-ELDs do not allow tuning of color emission but do have the advantage of a remarkable ~ 10X contrast between emission modes. Application of the simple SC-ELD structure to switching between other visible and/or infrared wavelengths is envisioned based on appropriate choice of RE dopants in the GaN layers.

5. Full color capability

One of the ultimate goals beyond multiple color capability based on GaN:RE is the prospect of full color (or white light) capability through additive light generation from integrated RGB ELDs or subtractive light generation from a codoped (GaN:Eu,Er,Tm) or stacked phosphor (GaN:Eu/GaN:Er/GaN:Tm). Regardless of phosphor layer format, the individual GaN:RE phosphors are ideal for full color capability since the spectra are characterized by sharp dominant peaks well-matched to the definition of saturated RGB [18] colors. This is a clear advantage for GaN:RE over many phosphors which have broad or multiple peak emission spectra which require filtering [4] in order to generate a saturated RGB color. The full color capability of GaN:RE ELDs is illustrated using the CIE chromaticity diagram shown in Fig. 5. The triangle in the diagram connects and defines the full color capability of emission from GaN doped with Tm (blue), Er (green), and Eu (red). For comparison, commercial II–VI TFEL phosphors and CRT phosphors are incorporated into the diagram also. The II–VI TFEL and CRT phosphors provide adequate full color capability. The color triangle defined by GaN:RE phosphors encapsulates almost all of the commercialized II–VI TFEL and CRT phosphors and provides superior color capability. Based on recent successes with orange GaN:Er,Eu and turquoise GaN:Tm,Er ELDs, we expect that proper mixing of RE dopants in a GaN:Er,Eu,Tm ELD should result in white light emission. Therefore, emission of any color is envisioned possible based on TFEL of GaN doped with multiple RE dopants.

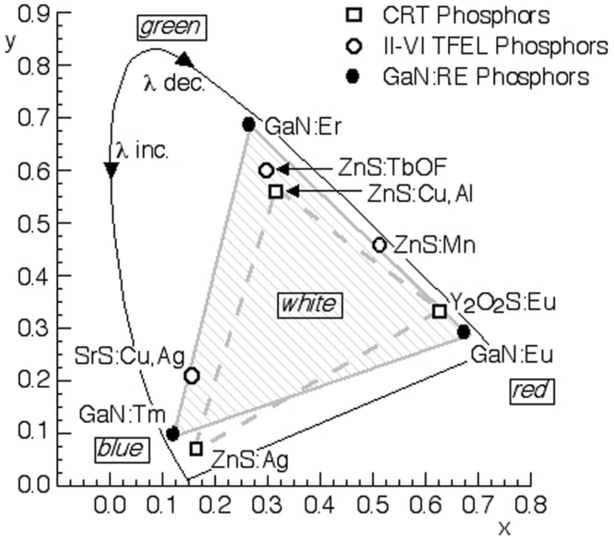


Fig. 5. CIE x–y chromaticity diagram showing the location of RGB GaN:RE ELDs (closed circles). Also shown are the coordinates of other commercial II–VI TFEL phosphors (open circles) and CRT Phosphors (open squares). In addition to primary colors, mixed colors or white light can be obtained by mixing relative intensities found within the triangle defined by the individually colored constituents.

6. Conclusion

In summary, we have reported on multiple color capability based on RE-doped GaN electroluminescence. GaN easily incorporates the trivalent RE atoms and can provide adequate hot carriers in order to excite RE emission that spans the visible spectrum. The phosphor systems exhibits excellent versatility in multiple color emitting devices.

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References

[1] A.J. Steckl, J. Heikenfeld, M. Garter, R. Birkhahn, D.S. Lee, Compound Semiconductor 6 (1) (2000) 48 and reference therein.
[2] H.J. Lozykowski, W.M. Jadwisienczak, I. Brown, J. Appl. Phys. 88 (1) (2000) 210 and reference therein.
[3] R. Mueller-Mach, G.O. Mueller, M. Leskelä, W. Li, M. Ritala, Electroluminescence II, in: G.O. Meuller (Ed.), Semicond. Semimetals, Academic Press, 2000.
[4] C.N. King, J. Vac. Sci. Technol. A 14 (3) (1996) 1729.
[5] S. Grossman, Electronic Design, May 1 (2000) p. 25.
[6] D.S. Lee, J. Heikenfeld, R. Birkhahn, M. Garter, B.K. Lee, A.J. Steckl, Appl. Phys. Lett. 76 (12) (2000) 1.
[7] J. Heikenfeld, A.J. Steckl, to be published.
[8] J.M. Zavada, M. Thaik, U. Hömmerich, J.D. MacKenzie, C.R. Abernathy, S.J. Pearton, R.G. Wilson, J. Alloy Compound 300-301 (2000) 207.
[9] J. Heikenfeld, D.S. Lee, M. Garter, R. Birkhahn, A.J. Steckl, Appl. Phys. Lett. 76 (11) (2000) 1365.
[10] R.D. Shannon, Acta Crystallogr., Sect. A: Cryst. Phys., Diffr. Theor. Gen. Crystallogr. 32 (1976) 751.
[11] D.R. Lide (Ed.), Handbook of Chemistry and Physics, CRC Press, 1997.
[12] P.H. Citrin, P.A. Northrup, R. Birkhahn, A.J. Steckl, Appl. Phys. Lett. 76 (20) (2000) 2865.
[13] E. Bellotti, I.H. Oguzman, J. Kolnik, K.F. Brennan, R. Wang, P.P. Ruden, Mat. Res. Soc. Symp. Proc. 468 (1997) 457.
[14] C.J. Summers, B.K. Wagner, W. Tong, W. Park, M. Chaichimansour, Y.B. Xin, J. Cryst. Grwth. 214-215 (2000) 918.
[15] P.D. Keir, C. Maddix, B.A. Baukol, J.F. Wager, B.L. Clark, D.A. Keszler, J. Appl. Phys. 86 (12) (1999) 6810.
[16] A.J. Steckl, M. Garter, D.S. Lee, J. Heikenfeld, R. Birkhahn, Appl. Phys. Lett. 75 (15) (1999) 2184.
[17] Y. Hamakawa, Appl. Surf. Sci. 92 (1996) 1.
[18] A. Bril, H.A. Klasens, Philips Res. Rep. 10 (1955) 305.