

Voltage-controlled yellow or orange emission from GaN codoped with Er and Eu

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Orange and yellow-colored light emission has been achieved at room temperature in the same electroluminescent device (ELD) made on GaN thin films codoped with Er and Eu. The GaN film was grown by molecular-beam epitaxy on Si (111) substrates using solid sources for Ga, Er and Eu and a plasma source for N₂. Simple Schottky devices were fabricated on the GaN films using indium-tin oxide (ITO) transparent electrodes. ELD spectra show that the yellow and orange colors result from the combination of green emission from Er (537, 558 nm) and red emission from Eu (621 nm). A color change was observed with applied bias, producing yellow at higher bias (−100 V) and orange at lower bias (−70 V). We have fabricated both relatively small (~250 μm) and large (1.45 mm) ELDs. Parameters for the chromaticity diagram were calculated to be $x=0.382$, $y=0.605$ for the yellow emission and $x=0.467$, $y=0.523$ for the orange emission. This work shows the possibility of achieving any intermediate color in the spectrum from green to red by adjusting the concentration of Er and Eu in GaN. © 2000 American Institute of Physics.
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Many efforts are underway to produce usable visible color emission using rare-earth (RE) materials. For this purpose, many host materials have been demonstrated such as fluoride glasses,^{1,2} sol-gels,³ ceramics,⁴ and semiconductors including Si.^{5,6} As far as semiconductors are concerned, II–VI host materials have been widely studied.^{7–9} III–V wide-band-gap semiconductors (WBGs) including GaN are known to have many advantages over other III–V compound semiconductors. This includes the fact that thermal quenching of the RE emission intensity is very low. GaN has been studied mainly for its optoelectronic application of infrared (IR) emission at 1.54 μm using Er doping.^{10,11} Moreover, GaN has other advantages as a host material for RE-based electroluminescent devices (ELD) since it is transparent to visible RE emission, and it is thermally and chemically rugged. We have recently reported¹² the first visible color emission using *in situ* doped GaN:RE ELDs. Emission of the three primary colors has been accomplished using the following rare earths: Er³⁺ doping for green^{12,13} light; Eu³⁺, Pr³⁺ doping for red^{14,15} light; Tm³⁺ doping for blue¹⁶ light. The rare-earth doping of GaN appears to be quite versatile,¹⁷ with mixed color emission being achieved and RE ion implantation also leading to visible emission. Recently, visible color emission from organic light-emitting diodes (LEDs)^{18,19} has been studied including yellow or orange color emission, but the emission spectra are much broader than those from rare-earth-doped GaN and the device structures being generally more complex. In this letter, we report orange and yellow emission obtained under different bias conditions from the same ELD fabricated on GaN thin films codoped with Er and Eu.

GaN films codoped with Er and Eu were grown in a Riber MBE-32 system on 2 in. *p*-Si (111) substrates. Solid

sources were used to supply the Ga, Er, and Eu fluxes, while an SVT Assoc. radio frequency (rf) plasma source was used to generate atomic nitrogen. For the nitrogen plasma, an rf power of 400 W and an N₂ flow rate of 1.5 sccm were used, yielding a chamber pressure of mid-10^{−5} Torr. The Ga cell temperature ranged from 870 to 885 °C and the equivalent pressure was 6–7 × 10^{−7} Torr. A GaN buffer layer was first deposited for 10 min at a substrate temperature of 600 °C. For the main growth, the substrate temperature was ramped to 800 °C, an initialization layer of undoped GaN was grown for 10 min and then a GaN:Er+Eu film was grown for an hour. The Er cell temperature was fixed at 820 °C, while the Eu cell temperature was varied from 340 to 370 °C for the growth of various films. The resulting average thickness of the GaN:Er+Eu layers was ~1.2 μm. For ELD fabrication, an ITO film (90% In₂O₃ and 10% SnO₂) was rf sputtered onto the GaN:Er+Eu to make optically transparent film contacts. Standard liftoff or etching procedures were used in ELD patterning. The ITO film was sputtered in a 100 W, 5 mTorr Ar plasma with a plasma induced dc bias of −200 V. After sputter deposition for 45 min and a 2 min anneal at 450 °C in an N₂ ambient, the main ITO film characteristics were: ~5000 Å thickness, ~5.5 Ω/square sheet resistance and greater than 85% transmission over the visible spectrum. The emission spectra were analyzed by an Acton Research spectrometer equipped with a photomultiplier sensitive in the ultraviolet-visible spectrum.

Electroluminescence (EL) characterization was performed using the ITO/GaN:Er+Eu ELDs resulting in excitation of Er³⁺ and Eu³⁺ luminescent centers in the GaN. The device operation was at room temperature, without a heat sink. Yellow emission was obtained at bias of −100 V and orange emission at −70 V from the same ELD as shown in Figs. 1(a) and 1(b), respectively. The dark notch in each figure is the probe tip used to supply voltage. The ELD area is 7.65 × 10^{−4} cm² and the ring width is 75 μm. The *I*–*V*

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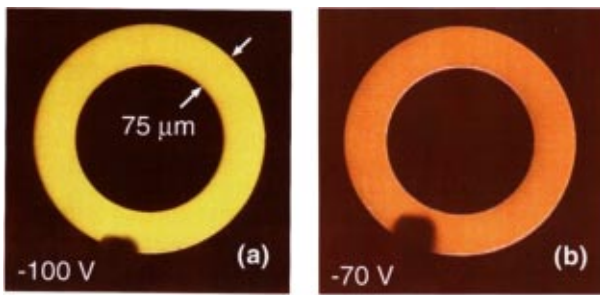


FIG. 1. (Color) Photograph of emission from a ring structure ITO/GaN:Er+Eu ELD with area of $7.65 \times 10^{-4} \text{ cm}^2$ and ring width of $75 \mu\text{m}$: (a) yellow emission at bias of -100 V ; (b) orange emission at bias of -70 V .

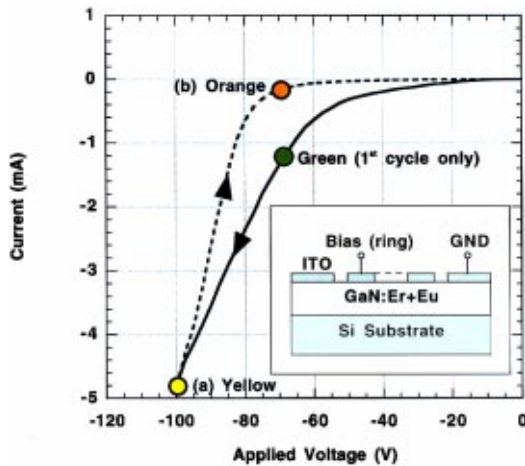


FIG. 2. (Color) $I-V$ characteristic of the ELD with increasing and decreasing voltages. Inset shows simple cross-sectional structure of the ELD.

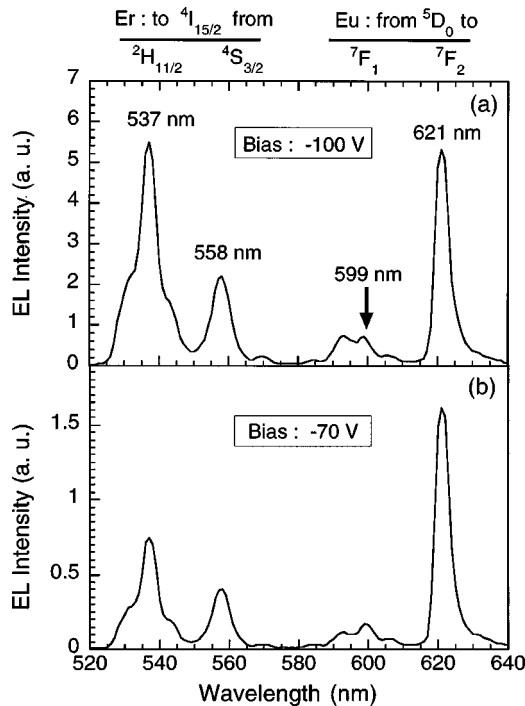


FIG. 3. EL spectra of (a) yellow emission at bias of -100 V , and (b) orange emission at bias of -70 V . At top of the figure the corresponding $4f$ inner shell transitions of Er^{3+} and Eu^{3+} are indicated.

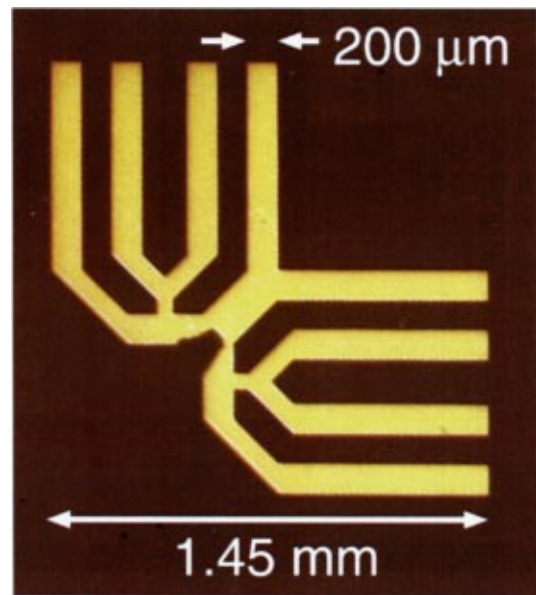


FIG. 4. (Color) Photograph of yellow emission from a large area ELD with the same ITO/GaN:Er+Eu structure.

characteristic of this device is shown in Fig. 2. The inset of Fig. 2 shows the simple structure of the ELD. Both bias (ring) and ground (large area, unpatterned) electrodes were formed on top of the GaN:Er+Eu film. It should be pointed out that the $I-V$ behaves differently during increasing and decreasing voltages, which resembles “hysteresis” in magnetic materials. ELDs being tested for the first time usually emit green light during increasing voltage until yellow emission is observed at around -100 V . At this point as the voltage is decreased, the ELD emission changes from yellow to orange. After this “first” cycle of applying voltage, however, ramping the bias produced a relatively stable behavior which gave orange emission at lower voltage and yellow emission at higher voltage, regardless of ramping direction. These “hysteresis-like” phenomena are not well understood

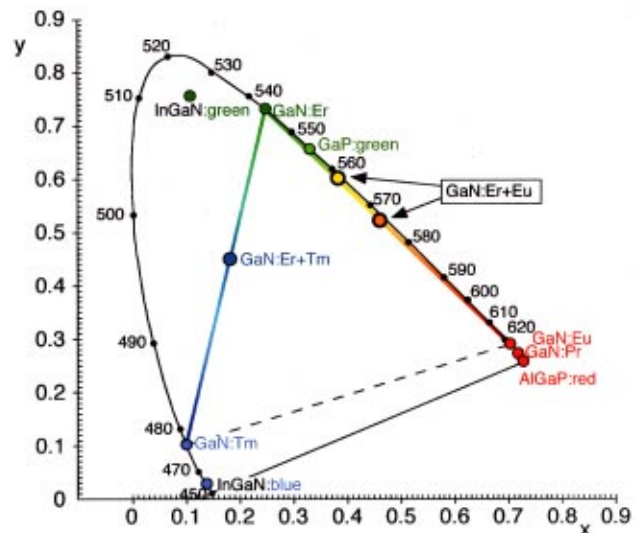


FIG. 5. (Color) CIE $x-y$ chromaticity diagram showing the location of the yellow and orange emission from the GaN:Er+Eu ELD with respect to the individual Er-doped and Eu-doped GaN ELDs. Also shown are the coordinates of mixed color emission using GaN:Er+Tm, of blue-emitting rare-earth GaN devices and red-emitting rare-earth GaN devices and of other commercial LEDs.

at this time and work is in progress to elucidate the mechanisms responsible for this effect.

EL spectra taken under corresponding bias conditions are shown in Fig. 3. The green peaks at 537 and 558 nm are attributed¹² to the Er^{3+} 4*f* inner shell transitions from the $^2H_{11/2}$ and $^4S_{3/2}$ levels to the $^4I_{15/2}$ ground level, respectively. The red peaks at 599 and 621 nm are attributed¹⁴ to the Eu^{3+} 4*f* inner shell transitions from 5D_0 to 7F_1 and to 7F_2 , respectively. The corresponding energies are listed in energy level diagrams found elsewhere.^{12,14} Figure 3(a) shows that for the yellow emission at bias of -100 V, the intensity of red lines from Eu was almost the same as that of green lines from Er. For the orange emission at bias of -70 V, Fig. 3(b) shows that the intensity of red lines was twice as high as that of green lines. Er-related green emission became stronger than Eu-related red emission at a bias level higher than -100 V. The observed color change resulted directly from different behavior of Er from Eu with applied voltage (and also current). The emission mechanism in our ELDs is believed to be impact excitation rather than electron-hole recombination.^{7,14,20} The impurity concentrations in the GaN were measured²¹ by Rutherford backscattering (RBS) channeling experiments. Er and Eu levels of 0.03 and 0.12 at. %, respectively, were measured. Also, some unintentional Mn doping was detected, of the order of ~ 0.01 at. %. Mn might have been present as an impurity in either the Er or the Eu source material. The presence of Mn could be a source of the ‘‘hysteresis’’ phenomenon, since Mn is well known as the cause of a similar hysteresis phenomenon in ZnS.²² Another possibility is the existence of Eu-related deep traps, which can also explain the high resistivity of our samples. The occurrence of divalent Eu ion (Eu^{2+}), possibly through electron transfer or impact ionization, was also considered but no Eu^{2+} -related broad emission was detected.²³

A larger area ELD is shown in operation in the yellow emission bias condition in Fig. 4. The bias condition was the same as that used in the smaller ring-shaped ELDs. The overall width of this ELD is 1.45 mm and consists of 200 μm lines. The uniform light emission seen in Fig. 4 shows the possibility of making larger devices or arrays of ELDs using this approach.

A first attempt was performed to place the yellow and orange color of the GaN:Er+Eu device on the Commission Internationale de l’Eclairage (CIE) *x-y* chromaticity diagram. We assumed that secondary wavelengths had no contribution to the overall color and that the color wavelengths acted as delta functions of intensity. Using the power measurements and the measured spectra, the chromaticity coordinates were calculated: $x=0.382$, $y=0.605$ for yellow color operation and $x=0.467$, $y=0.523$ for orange color operation. These coordinates were placed on the line between the green GaN:Er ELD and the red GaN:Eu ELD, as shown in Fig. 5. Also shown in Fig. 5 are the coordinates of mixed color

emission from GaN:Er+Tm ELDs and the red emitting rare earth-doped (Pr) GaN devices. CIE coordinates of other commercial devices are also shown for comparison.

In summary, yellow and orange emission has been achieved from ELDs fabricated on GaN thin film; codoped with Er and Eu. Both emissions were obtained from the same ELD, but at different bias conditions: yellow at -100 V and orange at -70 V. ‘‘Hysteresis’’-like phenomena were observed in the color-*V* and *I-V* characteristics and work to fully understand the phenomena is in progress. Both small (250 μm) and large (1.45 mm) ELDs were successfully fabricated. Chromaticity calculations show that the emitted colors were simple combinations of the colors emitted by the Er- and Eu- singly-doped GaN devices. This also shows that any intermediate color can be obtained by adjusting the Er and Eu relative concentrations.

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