

# Rare-Earth-Doped GaN Switchable Color Electroluminescent Devices

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**Abstract**—Switchable color (SC) light emission has been obtained from thin-film electroluminescent devices (ELDs) which use green Er- and red Eu-doped GaN phosphors. These two-electrode SCELDS can switch color through variation of applied bias. Different SCELDS structures, which share in common a stacked GaN:Er/GaN:Eu phosphor layer, can be implemented for use with dc or ac operation. A single SCELDS can emit green (537/558 nm), red (622 nm), yellow, and orange. For the DC-SCELDS, an electrically rectifying GaN/p-Si interface allows polarity-dependent current paths, which induce selective luminescence of red or green phosphor layers. For the AC-SCELDS, as the bias frequency is increased, bright red emission from GaN:Eu saturates while green emission from GaN:Er increases and becomes dominant. The AC-SCELDS exhibits brightness levels  $>10$  cd/m<sup>2</sup> and can change chromaticity coordinates by as much as  $\Delta x > 0.32$  and  $\Delta y > 0.33$ . Application of these devices to switching between other visible and/or infrared wavelengths is envisioned based on appropriate choice of luminescent dopants in the GaN layers.

**Index Terms**—Display, electroluminescence, GaN, phosphor, switchable color.

## I. INTRODUCTION

RESEARCH on light emitting devices which can change emission color by varying the electrical bias is of importance for multicolor flat panel displays, indicators and backlights. Commercialized approaches to obtaining multiple color capability are color-by-white [1], [2] (which uses a planar arrangement of red, green, and blue (RGB) color filters to subtractively create saturated RGB colors from white light) and techniques for integration of side-by-side single color RGB devices [2], [3], which produce additive multicolor emission. Multicolor capability has also been demonstrated by use of multiple electrical contacts to a stack of transparent single color devices such as organic light emitting diodes [4], [5] (OLEDs) or inorganic thin film electroluminescent devices [6] (ELDs). However, these are multicolor and multidevice structures, which require bias control of three or more electrodes.

A true switchable color (SC) device utilizes a generally less complex device structure requiring only two electrodes. Examples of SC devices are tunable [7], [8], color or switchable [9]–[11], color OLEDs, with the color change induced by the magnitude of applied voltage or by the polarity of the applied bias, respectively. In this paper, we report an *inorganic*

semiconductor-based SCELDS that can change between red, green, yellow, or orange emission by varying the electrical bias to only two electrodes. The SCELDS we report here are based on the rare earth-doped GaN phosphor system [12]. GaN has emerged as an excellent host [13] for visible [14] light emission from trivalent rare earths, which occupy substitutional sites on the Ga sub-lattice. In a flat panel display, the two-electrode SCELDS have the advantage of structural simplicity over their three-electrode counterparts. The SCELDS also have potential for switchable infrared [15] (IR) emission which would be useful in applications such as single-fiber multichannel optical communications. The emission colors are determined by the luminescent activators introduced, primarily rare earth or transition metals in a GaN-based phosphor layer. These dopants are impact-excited by hot carriers which are provided by a high electric field applied to the GaN layer. The SCELDS structures contain a stacked green/red phosphor layer which can be optimized for dc or ac operation. For the DC-SCELDS, an electrically rectifying GaN/p-Si interface allows polarity-dependent current paths which induce selective luminescence of red or green phosphor layers. For the ac-SCELDS, increasing the bias frequency results in saturation of the bright red phosphor emission, while the green phosphor emission increases and becomes dominant.

## II. DC-SCELDS

### A. DC-SCELDS Device Structure

The structure of the dc-biased SCELDS is shown in Fig. 1. For the DC-SCELDS, an Er- and Eu-doped GaN layered structure was grown in a Riber molecular beam epitaxy system on 2 in. p-Si (111) substrates of  $\sim 1\text{--}10$   $\Omega\text{-cm}$  resistivity. Ga, Er, and Eu solid sources were used in conjunction with a radio frequency plasma source supplying atomic nitrogen. The epitaxial growth sequence starts with  $\sim 300$  nm of undoped GaN, followed by  $\sim 300$  nm of GaN:Eu and 100 nm of GaN:Er. The Eu and Er concentrations utilized range from  $\sim 0.1$  to 1 at.%. After growth, indium–tin oxide (ITO) ring contacts were deposited by RF sputtering. During operation of the DC-SCELDS the ITO ring contact is always used as the (positive or negative) bias electrode with the other much larger ITO contact being grounded. Emission in either bias polarity occurs primarily under the bias electrode. The growth on p-Si (111) is important not only in supporting GaN epitaxy, but in creating a polarity-dependent current path through the structure, which is believed to be the primary reason for the switchable color emission.

Manuscript received December 27, 2001; revised June 13, 2002. This work was supported in part by ARO Contract DAA D19-99-1-0348. The review of this paper was arranged by Editor J. Hynecek.

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Publisher Item Identifier 10.1109/TED.2002.802663.

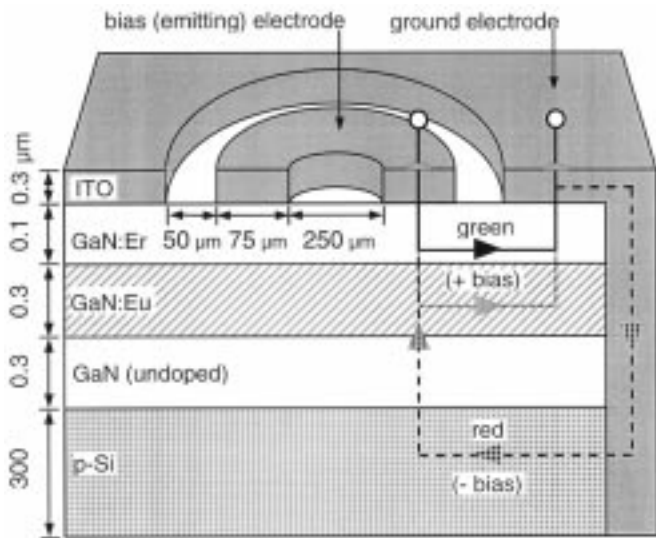


Fig. 1. Schematic diagram of the DC-SCELD structure and dominant current paths corresponding to positive (solid and dotted lines) and negative voltage (dashed line) applied to the emitting bias electrode.

### B. DC-SCELD Electro-Optic Characteristics

As shown in Fig. 2, the spectrum from the DC-SCELD switches between green (537/558 nm) and red (622 nm) emission based on the polarity of the applied bias. The emission is measured from an uncooled DC-SCELD with an emitting area of  $7.65 \times 10^{-4} \text{ cm}^2$ . The DC-SCELD exhibits  $\sim 10\times$  contrast between red and green emission modes and is capable of greater than  $10 \text{ cd/m}^2$  brightness at  $\sim 100 \text{ V}$ . Based on previous reports of red [16], [17] (Pr or Eu), green [18] (Er), blue [19] (Tm), and mixed color [20] (Er:Tm, Er:Eu) GaN ELs, proper choice of rare earth dopant in the GaN layers should allow for DC-SCELDs that switch between any two colors in the visible spectrum or at infrared wavelengths (such as the  $1.3$  and  $1.5 \mu\text{m}$  wavelengths emitted by Pr and Er, respectively). AC biasing of the DC-SCELD should result in a color mixing (yellow or orange) of each polarity associated color (red or green).

Current-voltage ( $I$ - $V$ ) characteristics shown in Fig. 3 indicate that current paths through the DC-SCELD change with bias polarity. When negatively biased, several milliamps of current flow through the DC-SCELD and red light is emitted (dashed line current path in Fig. 1). Under positive bias, the DC-SCELD has  $>10\times$  increase in series resistance and exhibits green light emission (solid line current path in Fig. 1). Either of these current paths can become dominant (regardless of bias polarity) if the GaN layer thickness and substrate conductivity are chosen accordingly [21]. For the DC-SCELD structure utilized, neither of these paths are strongly favored with respect to GaN layer thickness and substrate conductivity, allowing the current paths and  $I$ - $V$  characteristics to be dominated by the GaN/p-Si interface. The insert in Fig. 3 shows the rectifying nature of the GaN/Si interface through  $I$ - $V$  measurement of  $150 \text{ nm}$  GaN films on n- and p-Si. For the Fig. 3 insert plot, the GaN layer (semi-insulating) is  $\sim 4\times$  thinner than the combined GaN layers of the Fig. 3 main plot. Similar, but not identical,  $I$ - $V$  characteristics are seen from GaN/Si sample to sample. Slight variation in  $I$ - $V$  characteristics arises from repeatability limitations of GaN

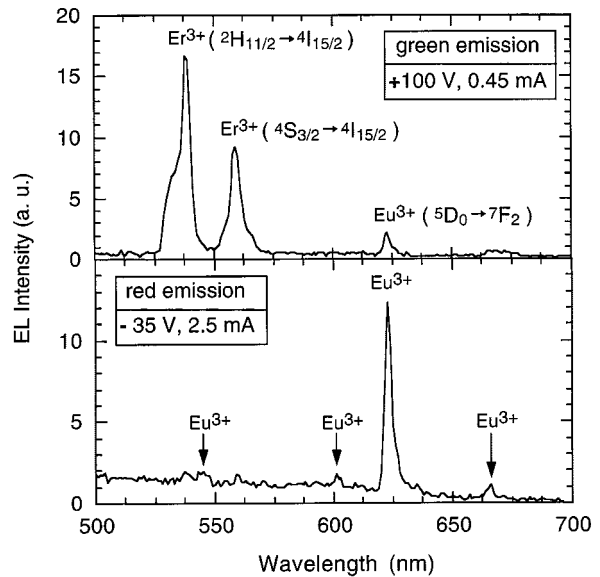


Fig. 2. EL intensity measured from ITO/GaN:Er/GaN:Eu/p-Si DC-SCELD for positive and negative bias applied to the ring electrode. Emission lines from GaN:Er and GaN:Eu are labeled and the dominant atomic transitions of the trivalent rare earth dopants are indicated.

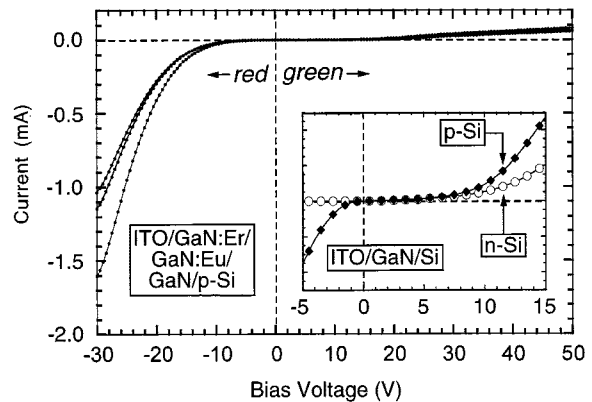


Fig. 3.  $I$ - $V$  characteristic of a DC-SCELD ( $700 \text{ nm}$  GaN:Er/GaN:Eu/GaN). The inset shows a current-voltage characteristic of a device structure with only  $150 \text{ nm}$  of undoped GaN grown on both p- and n-Si substrates.

MBE. However, it is clear that the substrate dopant type strongly controls the rectifying nature of the GaN/Si interface. To summarize, red emission is observed under negative bias since current flows vertically through the GaN:Er,Eu layers and effectively "shorts" to the conductive Si substrate/ITO ground electrode. Under positive bias, current flow is restricted to the GaN layers only and green emission results along with an increase in  $I$ - $V$  series resistance.

### C. DC-SCELD Proposed Device Mechanisms

Polarity dependence of current paths is believed to be the dominant mechanism behind the color switching behavior, but clearly cannot be the only mechanism giving rise to the high contrast between emission modes. Assuming the majority of voltage ( $30$ – $100 \text{ V}$ ) is applied to the semi-insulating GaN layers, the applied field strength is in the range of  $0.4$  to  $1.4 \text{ MV/cm}$ . According to theoretical calculations [22] of high field electron

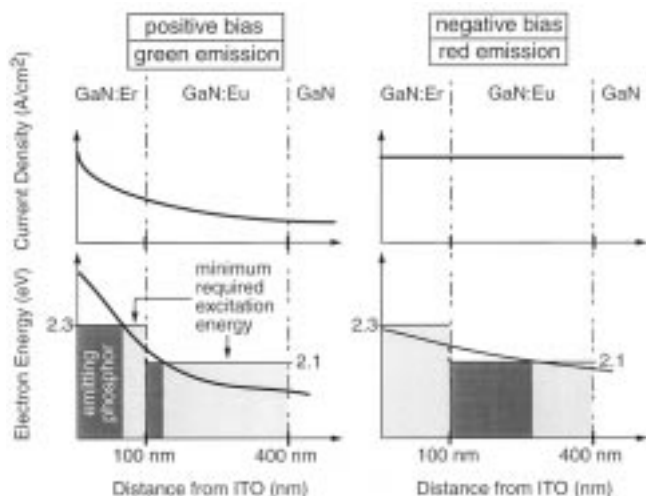


Fig. 4. Qualitative graphs of polarity-dependent current density versus distance into the phosphor layers (top graphs) and polarity-dependent electron energy versus distance into the phosphor layers (solid line bottom graphs). The threshold energies for red (2.1 eV) and green (2.3 eV) phosphor excitation are also shown. Phosphor regions with carriers sufficiently hot for phosphor excitation (emission) are shown in dark gray whereas unexcited phosphor regions are shown in light gray.

transport in GaN, the majority of hot carriers begin to gain adequate energy for impact excitation ( $>2$  eV) at applied fields of  $\sim 1$  MV/cm. Therefore, under device operating voltages of 30–100 V (0.4 to 1.4 MV/cm), the efficiency of excitation of the GaN:Er and GaN:Eu phosphor layers should be highly sensitive to any local variations in field strength. Beyond polarity dependent current paths, there are very likely additional mechanisms which involve the localization of hot carriers to either the red or green phosphor layers. Qualitative graphs of the current density and electron energy versus depth for positive and negative bias are shown in Fig. 4. As represented in Fig. 4, energy barriers and/or band bending in the vicinity of interfaces between layers could lead to a local increase in electric field and increased rare earth impact excitation. The dominance of red emission observed during negative bias could also be attributed to a lower threshold energy for impact excitation of GaN:Eu ( ${}^5D_0$  level or  $\sim 2.1$  eV) in comparison to GaN:Er ( ${}^2H_{11/2}$  level or  $\sim 2.3$  eV). Another contrast mechanism could be tied to the resistivities of the rare earth-doped GaN layers. If the GaN:Eu is more resistive than the GaN:Er layer, under positive bias the lateral current between the ITO electrodes will be mostly confined to the less resistive GaN:Er layer and will result in primarily green luminescence. Under negative bias, current travels vertically through both GaN:Er and GaN:Eu layers and the more resistive GaN:Eu layer would experience a higher field strength and subsequent hotter electron distribution than the one found in the GaN:Er layer. The individual resistivities of the GaN:Er and GaN:Eu phosphor layers can not be easily measured in the finished DC-SCELD or predicted with strong confidence due to slight variances in the epitaxy process. Therefore, the effect of phosphor layer resistivity is noted as at least a theoretically possible contrast enhancement approach, if not an already existing mechanism in the DC-SCELD. Characterization of poly-crystalline high-field EL devices is very difficult due to a limited ability to apply conventional semiconductor theory

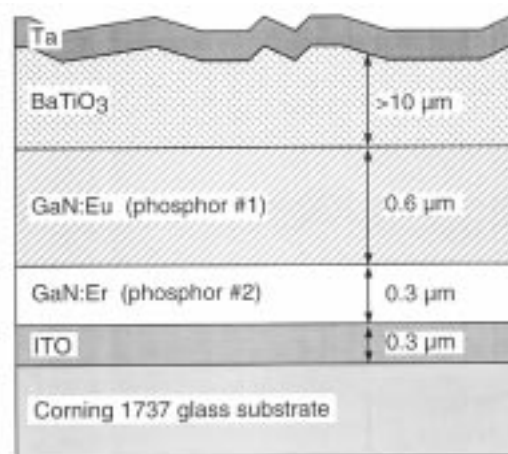


Fig. 5. Schematic diagram of the AC-SCELD structure formed on glass substrates. The high permittivity ( $\epsilon > 500$ ) dielectric layer capacitively couples an alternating voltage to the stacked GaN:Eu/GaN:Er phosphor layer.

based on low-field conditions and highly crystalline semiconductors such as Si. However difficult to characterize, high-field EL phosphors are efficient light emitters (up to  $\sim 5$  lm/W) and a mature technology for which further understanding is presently needed and being pursued. For the DC-SCELD demonstrated in this work, it is the present understanding that the polarity controlled current density, electron energy, and phosphor threshold likely combine to determine the DC-SCELD color contrast.

### III. AC-SCELD

#### A. AC-SCELD Device Structure

AC-ELDs based on II–VI phosphors [23], [24] are commercially utilized in flat panel display applications calling for extreme ruggedness and reliability [25]. Also, II–VI phosphor AC-ELDs on ceramic substrates are being pursued [26] for applications such as flat-TVs. AC-ELDs can be biased with inexpensive ( $\sim \$2$  U.S.) drivers, which can supply voltages up to 200 V or greater. The second type of SCELD demonstrated here is shown in Fig. 5 and utilizes a novel AC-ELD structure [27], which we have developed. This device can selectively emit red, green, yellow, or orange light. Our approach is similar to a previous report of an AC-SCELD structure [28] based on II–VI phosphors, which, however, had a much more limited color gamut (yellow or green).

AC-ELD (single color) and AC-SCELD (switchable color) structures were formed on Corning 1737 glass substrates, which have a thermal strain point of  $666$  °C, sufficiently above the  $\sim 600$  °C substrate temperature at which GaN:Er and GaN:Eu phosphors were deposited. Corning 1737 is a widely utilized display glass [29] due to its compatibility with low temperature ( $500$ – $600$  °C) poly-Si processing used for active-matrix liquid crystal displays. GaN:Eu ( $\sim 1$   $\mu\text{m}$ ), GaN:Er ( $\sim 1$   $\mu\text{m}$ ), and layered GaN:Eu ( $\sim 0.6$   $\mu\text{m}$ )/GaN:Er ( $\sim 0.3$   $\mu\text{m}$ ) phosphor films were deposited by molecular beam epitaxy onto  $\sim 300$  nm ITO-coated 1737 glass substrates. Following phosphor deposition, two layers of Dupont 5540 dielectric paste were screen printed. The 5540 paste contains BaTiO<sub>3</sub> along with glass or

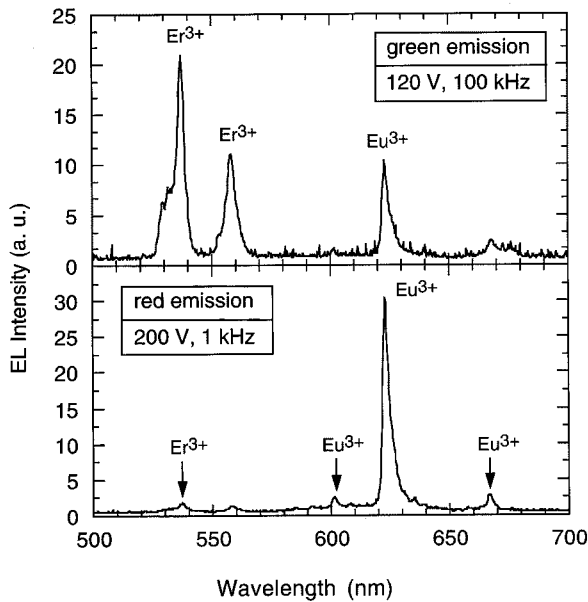


Fig. 6. EL intensity measured from Ta/BaTiO<sub>3</sub>/GaN:Eu/GaN:Er/ITO/1737 glass substrate AC-SCELD for high (100 kHz) and low (1 kHz) frequency. Emission peaks from GaN:Er and GaN:Eu are labeled.

fluxing agents that facilitate low temperature (<900 °C) sintering of the dielectric. To preserve compatibility with the glass substrate a special printing/firing sequence for the dielectric layer was implemented in order to significantly alleviate substrate shrinkage and warpage. The resulting dielectric layer had a thickness of  $\sim 40 \mu\text{m}$ , a breakdown strength  $>300 \text{ V}$ , and a permittivity of  $\epsilon \sim 500\text{--}1000$ . The back electrode is formed by  $\sim 300 \text{ nm}$  Ta sputtering and stencil mask patterning of 5-mm diameter dots.

### B. AC-SCELD Electro-Optic Characteristics

The completed AC-SCELD structure exhibits bias-controllable (voltage and frequency) emission color which ranges from red to green and all colors in between (various shades of yellow and orange). A strong contrast between the absolute intensity of green and red emission modes is shown in emission spectra plotted in Fig. 6. In the green emission mode, the emission color appears as a saturated green despite the presence of a moderately strong red peak from GaN:Eu. The photopic response of the human eye to the AC-SCELD color change is accounted for in the Commission Internationale d'Éclairage (CIE) color space of Fig. 7. In Fig. 7, the color change is induced by varying the square wave peak voltage from 120 V to 200 V, and the bias frequency between 1 and 100 kHz. The luminance and chromaticity measurements were performed with a Minolta CS-100 Chroma-Meter. Changes in frequency or voltage both produce strong color change. The color change can also be induced at constant input power or brightness ( $\sim 10 \text{ s cd/m}^2$ ) by utilizing high voltage, low frequency biasing to produce red emission, and utilizing low voltage, high frequency biasing for green emission. The high frequency biasing should use a low duty cycle to reduce the power input, i.e., high frequency ( $>10 \text{ kHz}$ ) biasing for short durations ( $<1 \text{ ms}$ ).

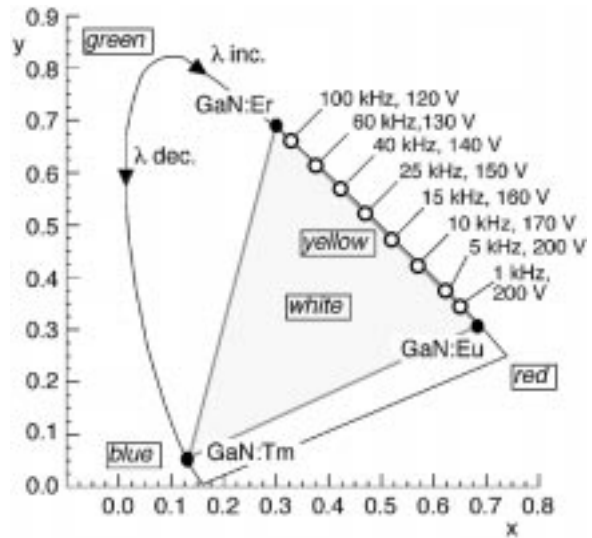


Fig. 7. 1931 CIE  $x$ - $y$  chromaticity diagram showing the color change induced in a GaN:Eu/GaN:Er AC-SCELD. Also shown is the overall color capability of the GaN:Tm, Er, or Eu phosphor systems. In addition to primary colors, mixed colors or white light can be obtained by mixing relative intensities found within the triangle defined by the individually colored constituents. A single AC-SCELD is capable of red, green, yellow, or orange color emission. The square wave frequency and peak voltage is listed for each color obtained.

### C. AC-SCELD Device Mechanisms

The AC-SCELD device structure shown in Fig. 5 was designed with the following criteria in mind. Phosphor layer #1, which demonstrates a higher luminance at a given voltage, should have a relatively long emission lifetime ( $\tau_1$ ), which results in saturation of emission intensity as the bias frequency exceeds  $1/\tau_1$ . Phosphor layer #2, which has a lower luminance at the same voltage, should have a comparatively short emission lifetime ( $\tau_2 \ll \tau_1$ ) so that emission intensity increases linearly with frequency. When these two phosphor layers are combined in a single AC-SCELD, phosphor #1 will dominate the emission intensity at lower frequencies, whereas at higher frequencies, the shorter lifetime phosphor #2 should dominate the emission intensity, and therefore color. Luminance versus applied square wave peak voltage and frequency are shown in Fig. 8. The data in Fig. 8 is taken from AC-ELDs which utilize *single*  $\sim 1 \mu\text{m}$  thick phosphor layers of either GaN:Eu for red emission or GaN:Er for green emission. GaN:Er and GaN:Eu phosphors meet the basic AC-SCELD requirement since GaN:Eu is roughly twice as bright ( $30 \text{ cd/m}^2$ ) as GaN:Er ( $13 \text{ cd/m}^2$ ) at 1 kHz, 200 V applied bias. Furthermore, photoluminescent [30] and electroluminescent measurements reveal that GaN:Eu has an emission lifetime ( $\tau_1 \sim 250 \mu\text{s}$ ) more than an order of magnitude longer than the emission lifetime [31] for GaN:Er ( $\tau_2 \sim 7 \mu\text{s}$ ). Electroluminescent lifetime, which is approximated as  $1/e$  of the maximum EL intensity, is shown in Fig. 9 for GaN:Eu and GaN:Er AC-ELDs. The AC-ELDs were biased with a 100 Hz 200 V<sub>p</sub> square wave for which excitation occurs during the rising/falling edge of the square wave (slew rate  $\sim 100 \text{ V}/\mu\text{s}$ ). The EL intensity is filtered with a diffraction grating to  $<1 \text{ nm}$  resolution and detected by a photomultiplier tube with an electron transit time of  $<22$

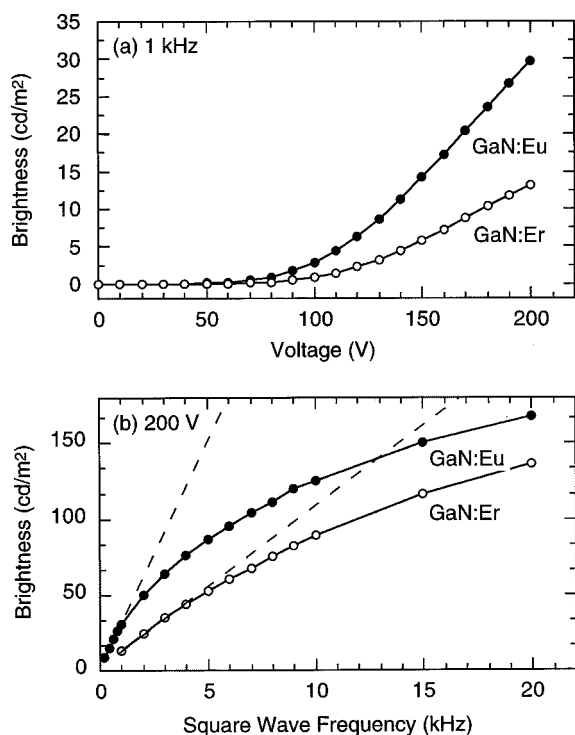


Fig. 8. (a) Luminance–voltage plots at 1 kHz from separate Ta/BaTiO<sub>3</sub>/phosphor/ITO/1737 glass substrate AC-ELDs with GaN:Eu or GaN:Er phosphor of  $\sim 1 \mu\text{m}$  thickness. (b) Luminance–frequency plots at 200 V square wave peak voltage from AC-ELDs with GaN:Eu or GaN:Er phosphors. The dotted lines in (b) represent the expected linear luminance rise without saturation due to emission lifetime. The onset of frequency saturation occurs in the range of 1 kHz for GaN:Eu and 10 kHz for GaN:Er.

ns. Fig. 8(b) demonstrates that the GaN:Eu emission intensity begins to saturate [32] at a lower frequency than GaN:Er emission. One method to identify the onset of saturation is by calculating the 3 dB reduction from the linear relation. The 3 dB reduction is observed for GaN:Eu at  $\sim 1$  kHz and for GaN:Er at  $\sim 10$  kHz, which supports the emission lifetime argument.

The dependence of emission color on frequency and voltage is plotted in Fig. 10. The ordinates of Fig. 10(a) and (b) are the 1931 CIE  $x$  and  $y$  coordinates. The emission color is observed to be red shifted by 0.05–0.08 CIE in both  $x$  and  $y$  CIE coordinates at all bias voltages as the frequency is reduced from 50 kHz to 10 kHz. This is in agreement with the emission saturation argument concluded from Figs. 8(b) and 9. At a fixed frequency of 10 or 50 kHz the emission color is red shifted by a somewhat larger amount of  $>0.10$  in both  $x$  and  $y$  as the peak voltage is increased from 140 V to 200 V. By adjusting both voltage and frequency the AC-SCELD changes CIE chromaticity by a total of  $\Delta x > 0.32$  and  $\Delta y > 0.33$ . For an AC-SCELD, charge transport across, and therefore impact excitation of, the phosphor layer occurs only as the capacitive structure charges up ( $Q = CV$ ). The red-shift in color with increasing voltage (shown in Fig. 10) is clearly not due to current saturation ( $I = C \cdot dV/dt$ ) of emission since this would result in a green color shift with increasing voltage based on the emission saturation with frequency argument concluded from Figs. 8(b) and 9. The increase in red color with additional peak

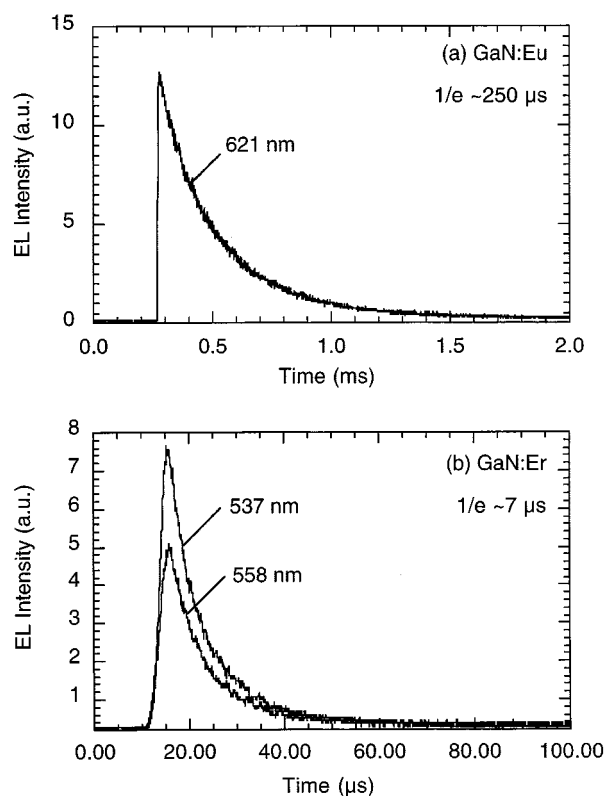


Fig. 9. EL intensity versus time for GaN:Eu and GaN:Er AC-ELDs. The AC-ELDs were biased at 100 Hz and 200 peak voltage. Phosphor excitation occurs during the rising/falling edge of the square wave (slew rate  $\sim 100 \text{ V}/\mu\text{s}$ ). The EL intensity is filtered with a diffraction grating to better than 1-nm resolution and detected by photomultiplier tube with an electron transit time of less than 22 ns.

voltage is understood in terms of asymmetric charge injection [33] (injection from ITO/GaN versus from BaTiO<sub>3</sub>/GaN). This understanding was confirmed by showing that the chromaticity shift with increasing voltage is dependent on which phosphor layer (red or green) is adjacent to the BaTiO<sub>3</sub> layer. In a device in which the dopant order was switched, such that we have GaN:Er for phosphor #1 and GaN:Eu for phosphor #2, the effect of increasing bias voltage now resulted in a green shift. In addition to charge injection from the phosphor/dielectric interface, high permittivity dielectrics [33] such as BaTiO<sub>3</sub> are known to have the ability to inject charge from bulk traps within the dielectric. The amount of charge injection from the bulk dielectric increases with applied field (positive voltage on ITO) and should result in electrons with very high energy as they transit the GaN/BaTiO<sub>3</sub> heterojunction and inject into the GaN phosphor layer. These “hotter” electrons more efficiently excite the phosphor layer adjacent to BaTiO<sub>3</sub> than the phosphor layer adjacent to ITO, since after injection into the phosphor layer with higher energy, the electrons rapidly “cool” to the energy associated with nominal high field transport across the phosphor layer.

Switching the color (from red to green) by increasing the bias frequency increases the power input to and, of course, the luminance of the device. To counteract this effect, one can reduce the bias voltage. This would not only minimize any increase in input power, but would also maintain the same luminance level for

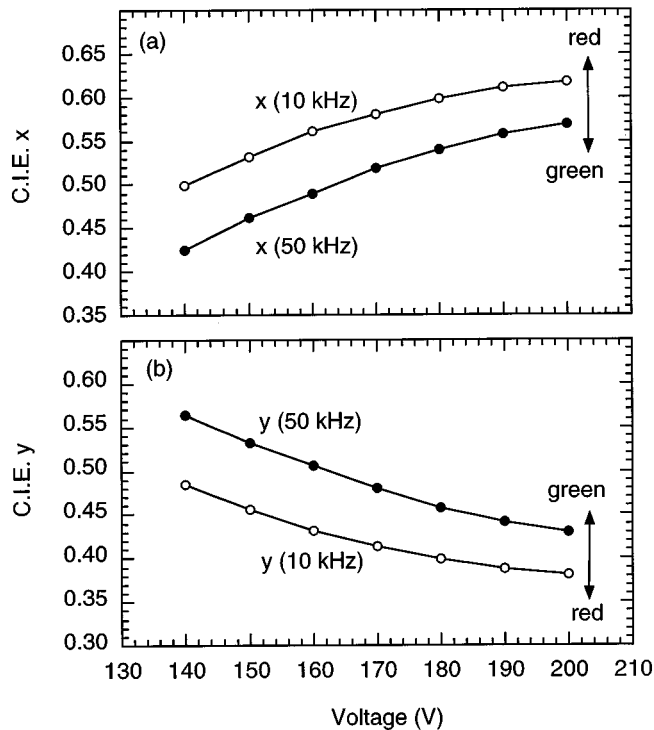


Fig. 10. The 1931 CIE (a)  $x$  and (b)  $y$  color coordinates versus voltage for square wave frequencies of 10 kHz and 50 kHz applied to an AC-SCELD. The emission color is red shifted by  $>0.05$  CIE  $x$  and  $y$  for all voltages as the frequency is reduced from 50 kHz to 10 kHz. The emission color is red shifted by  $>0.10$  CIE  $x$  and  $y$  at both 10 and 50 kHz as the peak voltage is increased from 140 V to 200 V.

the two colors. Voltage reduction also results in a reinforcement of the red-to-green color shift, as shown in Fig. 10. This effect points out the need to design the device such that the effects of frequency and voltage can balance each other. This design approach is properly implemented in the AC-SCELD shown in Fig. 5.

#### IV. CONCLUSIONS

In summary, we have reported on a versatile device structure for switching color emission based on Er- and Eu-doped GaN electroluminescence. For the DC-SCELD, it is believed that the electrically rectifying GaN/p-Si interface allows polarity dependent current paths which induce luminescence of distinct phosphor layers. These results should be extendable to a DC-SCELD, which switches between any two colors in the visible spectrum and several infrared wavelengths based solely on choice of rare earth dopant in the GaN layers. For the AC-SCELD, as the bias frequency is increased bright red emission from GaN:Eu saturates as green emission from GaN:Er increases and becomes dominant. The results for the AC-SCELD should be extendable to use of II-VI and oxide based phosphors, as long as the activator dopants (rare earth or transition metals) have a strong difference ( $10\text{--}100\times$ ) in emission lifetime and therefore frequency saturation. The SCELDs relieve difficulties of integrating red and green emitters on a single substrate, while requiring the use of only one additional biasing scheme for each color that is to be added (from the set of green, yellow, orange, or red).

#### ACKNOWLEDGMENT

The authors would like to thank D. S. Lee and M. Garter for their assistance with phosphor growth and DC-ELD fabrication, respectively. They would also like to acknowledge the support and encouragement of M. Gerhold and J. Zavada.

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