

# GaN:Eu electroluminescent devices grown by interrupted growth epitaxy

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## Abstract

In this paper we report on electroluminescent devices fabricated using Eu-doped GaN films grown by interrupted growth epitaxy (IGE). IGE is a combination of conventional molecular beam epitaxy and migration enhanced epitaxy. It consists of a sequence of *ON/OFF* cycles of the Ga and Eu beams, while the  $N_2$  plasma is kept constant during the entire growth time. IGE growth of GaN:Eu resulted in significant enhancement in the Eu emission intensity at 620.5 nm. The nitridation of the surface that occurs during the *OFF* cycle appears to be the dominant process producing the enhancement. Thick dielectric devices fabricated on glass substrates using IGE-grown GaN:Eu have resulted in luminance of  $\sim 1000$  cd/m<sup>2</sup> and luminous efficiency of  $\sim 0.15$  lm/W.

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## 1. Introduction

Inorganic electroluminescent devices (ELDs) have been a leading technology [1,2] for flat panel displays (FPD) requiring bright and robust displays operating under a wide range of conditions (e.g. temperature, ambient lighting, exposure to radiation, chemicals etc.). Recently, full color and large area FPD using ELD technology have been announced [3] for the high definition television (HDTV) market. ELDs use either thin film EL (TFEL) or thick dielectric EL (TDEL) device structures which incorporate a phosphor layer separated from top to bottom electrodes by two insulating layers. We have investigated [4,5] the family of trivalent rare earth ( $RE^{3+}$ ) doped GaN phosphors and have developed [6] TDEL devices producing red, green and blue saturated color emission and prototype FPDs.

In this paper we demonstrate ELDs fabricated with a novel growth procedure that significantly improves luminance and efficiency. We have modified conventional molecular beam epitaxy (MBE) by cycling the group III beams (Ga, Al,  $RE^{3+}$ ) on and off while maintaining a constant group V beam (N). We have named this technique interrupted growth epitaxy (IGE). This growth technique has been applied to GaN:Eu red

emitting phosphors in this current work, but IGE should also be applicable to other rare earth elements (Er, Tm, etc.) in many III–V semiconductors (InAlGa<sub>n</sub>, GaAs, InP, etc.) and possibly to transition metals in II–IV (ZnS, SrS, etc.) semiconductors. GaN:Eu IGE has resulted in significant emission enhancement in GaN:Eu films grown in conjunction with both silicon and glass substrates. In this paper, we discuss GaN:Eu IGE on (111) Si and glass substrates and characteristics of TDEL devices on glass were achieved through this technique.

## 2. Experimental procedure

The GaN:Eu phosphor deposition took place in a Riber MBE system utilizing solid sources for group III and rare earth elements and an RF plasma source for nitrogen. In conventional MBE all molecular beams are incident upon the growth surface simultaneously throughout the entire period and growth occurs continuously during the operation time. Furthermore, the constituent atoms and molecules are deposited on to the substrate preferably under stable group V conditions. In the case of MBE growth of GaN, both Ga and N shutters are open simultaneously. The small nitrogen radical lifetime on the surface allows only for very rapid reaction of Ga and N and immediate formation of GaN crystals [7]. Therefore the MBE growth technique frequently results in the formation of large

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number of GaN islands on the substrate surface due to the severe limitations in Ga atom migration on the surface at the relatively low MBE growth temperatures [8,9].

Several techniques have been investigated in order to enhance the quality of the semiconductor material, namely shutter control method [10], nitrogen beam modulation [1], and migration enhanced epitaxy (MEE) [11]. All these techniques have as a common feature the goal of increasing the surface migration of Ga atoms during GaN growth. In the first two techniques the nitrogen flux is interrupted periodically at a constant Ga flux to facilitate the surface migration of the Ga atoms. In this case the nitrogen shutter is modulated at periods in the order of seconds ( $\sim 1\text{--}2$  [12] and  $20\text{--}40$  s [10]). In migration enhanced epitaxy both Ga and N fluxes are modulated consecutively. In some cases the Ga shutter open time would coincide with the nitrogen shutter closed period without any interval of overlap [13]. MEE growth improvements are less pronounced at higher growth temperatures where the Ga atoms have higher surface mobility. Horikoshi [14] provides an excellent review of the MEE growth technique. In contrast, in IGE relatively long periods (from a few minutes to tens of minutes) of growth are used where all beams are incident on the substrate followed by periods where only selected beams are incident.

It is well known in the growth of III-N materials that the efficiency of group V material incorporation into the film is much less than that of group III, which results in films with a low V/III ratio. The IGE technique is designed to eliminate this problem, with the GaN film being periodically exposed to the nitrogen beam only while the growth is interrupted. The film growth is therefore accomplished in a periodic fashion, with the shutters of group III elements being open (*ON*) for a part of the cycle and closed (*OFF*) during the rest of time. The group V beam was on throughout the entire IGE cycling time.

The different group III cycling sequences employed to evaluate the IGE technique are shown in Fig. 1. Each duo of dark and light horizontal bars represents a different growth condition. The continuous light colored bars represent the flow of group V elements whereas the dark periodic bars represent flow of group III elements. The sequence with a 60-min group III cycling time has both group III and V continuously flowing for the entire duration as is the case in a conventional MBE growth (i.e. all shutters simultaneously open). All other growth sequences utilized a 5-min group III *OFF* time (i.e. only group V is on) introduced between consecutive group III *ON* cycles. The total group III *ON* time for all sequences is kept constant at 60 min.

These growth sequences were designed with the assumption that the growth of material occurs only during the time period when both group III and V shutters were open. The loss of material through dissociation during the group III *OFF* period is essentially negligible, as indicated by a roughly constant growth rate for all films ( $\sim 0.7$   $\mu\text{m/h}$ ) on Si substrates. During the group V only period several effects can occur: nitridation of the GaN surface, thermal annealing, etc. MBE parameters for the GaN:Eu growth were Ga cell at  $895$   $^{\circ}\text{C}$  with a beam equivalent pressure of  $\sim 5.5 \times 10^{-5}$  Pa and Eu cell at  $470$   $^{\circ}\text{C}$ .

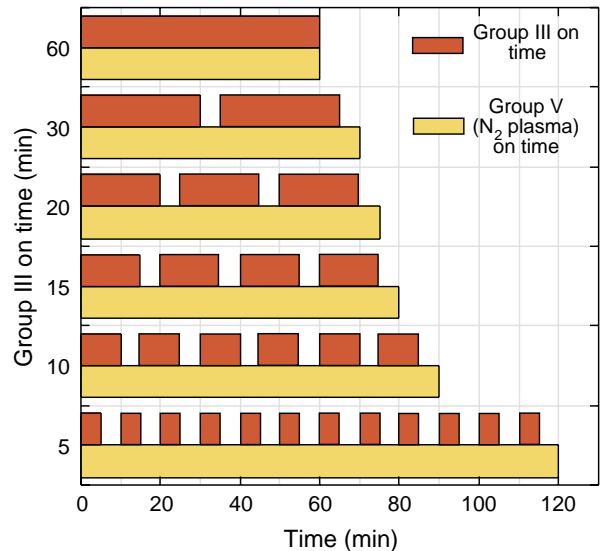


Fig. 1. Group III cycling time for different interrupted growth (IGE) MBE samples. The nitrogen plasma is continuous throughout each cycle, while the group III fluxes are switched *ON* and *OFF* periodically.

The Eu incorporation in the films was  $\sim 0.5$  at.%, which is below the onset of luminescence concentration quenching [7]. Since the surface temperature where growth occurs cannot be directly measured, we have used the temperature indicated by a thermocouple placed in contact with the rear of the sample holder to control the temperature of the growth process. The growth was carried out at  $800$   $^{\circ}\text{C}$  thermocouple temperature for glass substrates and  $650$   $^{\circ}\text{C}$  for Si substrates. Ceramic back plates were used for maximum heat transfer to the glass substrate. Even though the ceramic plates greatly improve the heat transfer there was no evidence that the actual surface temperature of the glass substrate reached the strain point (beyond which stress developed during cooling will be permanent) of  $666$   $^{\circ}\text{C}$ . The nitrogen plasma source was set at a gas flow of  $2.0$  sccm with  $400$  W forward RF power in order to achieve the stoichiometric growth condition. The stoichiometric growth condition for GaN:RE growth on glass substrates were determined through the optimization of the growth parameters. A very thin ( $\sim 10$  nm) AlN buffer layer was grown before the main GaN:Eu growth. We have observed that thin AlN buffer layers lead to improved GaN:Eu films on glass substrates. In order to protect the GaN:Eu layer an AlN capping layer was grown following the main layer growth.

### 3. Material characterization

After growth, the first evaluation of material quality as an EL phosphor is photoluminescence (PL). The PL characterization is carried out at room temperature using  $325$  nm photons from a He–Cd laser. In this “above-bandgap” PL, electron-hole pairs are photogenerated within the GaN:Eu material with an absorption depth of  $\sim 1$   $\mu\text{m}$ . Subsequently, the energy of the photogenerated carriers is transferred to Eu centers in the GaN host causing their transition to an excited state from which they can relax by the emission of photons of well defined energies [15].

Fig. 2 contains PL spectra for GaN:Eu films at various IGE cycling times on (111) Si (Fig. 2a) and glass (Fig. 2b) substrates. No GaN band edge emission (at  $\sim 365$  nm) is observed for films on either substrate. The absence of GaN band edge emission is probably caused by a combination of effects: (a) efficient transfer of energy from the host to the Eu ions followed by radiative relaxation; (b) reduced crystallinity in the GaN layer due to Eu doping and to the relatively low temperature growth necessitated by the glass substrates (as compared to growth on sapphire or SiC substrates for conventional GaN devices). PL emission from Eu-doped GaN films grown on Si has occasionally [16] included relatively weak near GaN band edge emission. The main features of the spectrum are a series of sharp lines at red wavelengths due to Eu emission. The most prominent emission peaks are at 621 and 632 nm, which correspond to the Eu intra-4f transitions  $^5D_0 \rightarrow ^7F_2$  and  $^5D_1 \rightarrow ^7F_4$  (tentatively assigned), respectively. Clearly the IGE growth technique has a strong influence on the Eu emission

intensity. Comparing, for example, the intensity of the  $^5D_0 \rightarrow ^7F_2$  transition at 621 nm from the sample grown on Si substrate at 60 min group III *ON* time (equivalent to the conventional MBE) to the sample with 20 min *ON* time, we can see that the latter has more than  $2\times$  higher peak intensity. The IGE effect is more pronounced for growth on Si substrates than for samples grown on glass. For GaN:Eu films grown on glass the highest overall increase ( $\sim 30\%$ ) in the 621 nm peak is obtained for the 15 min *ON* time sample. There are several possible explanations for the effect caused by the substrate during IGE growth: (a) structural differences in films grown on crystalline vs. amorphous substrates; (b) location of  $\text{Eu}^{3+}$  ions at different site environments.

In addition to the main peaks, several minor PL peaks are observed in Fig. 2 at wavelengths from  $\sim 540$  to  $\sim 665$  nm. The most prominent minor peaks are at  $\sim 600$  and 663 nm. Close examinations of minor peak intensities have displayed similar trends as the major peaks in the variations of their intensities

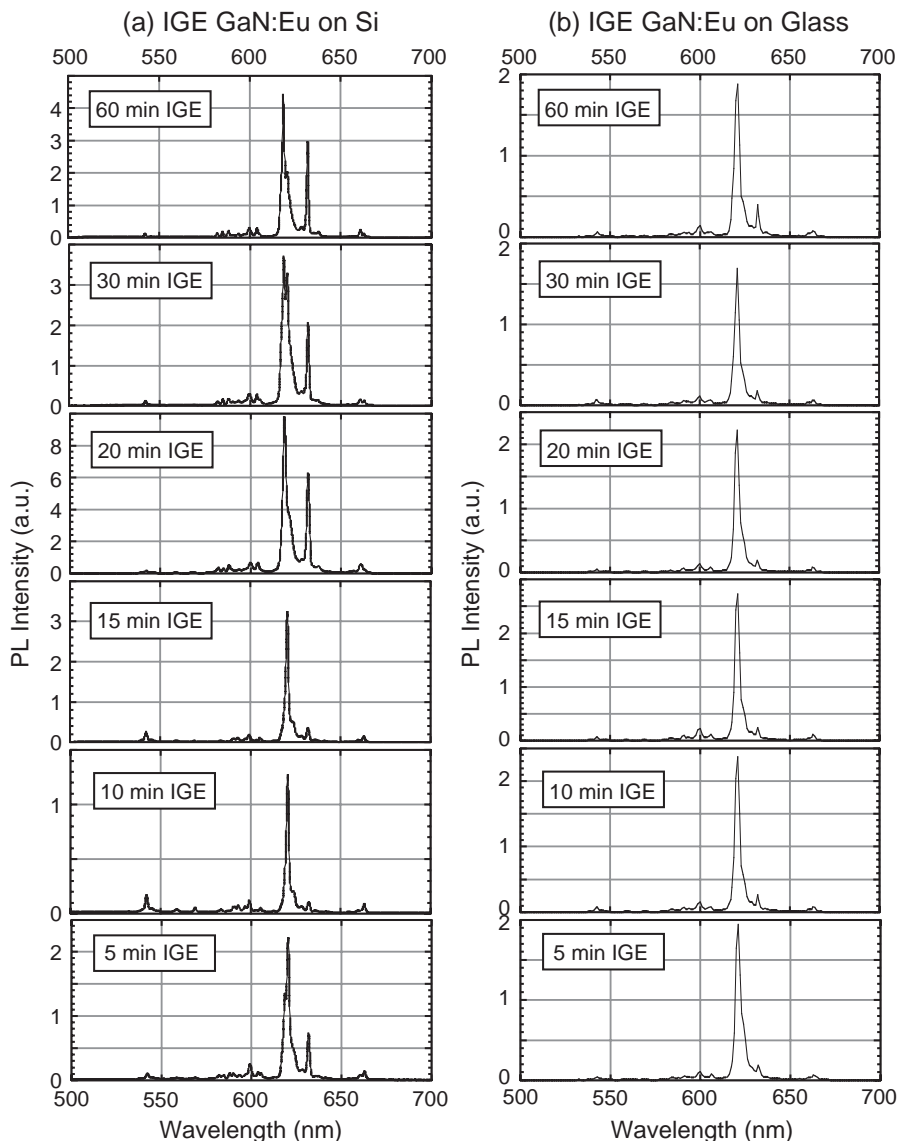


Fig. 2. Photoluminescence spectra of samples grown using various IGE *ON* times on Si (a) and glass (b) substrates. PL was measured at room temperature under 325 nm He–Cd laser excitation.

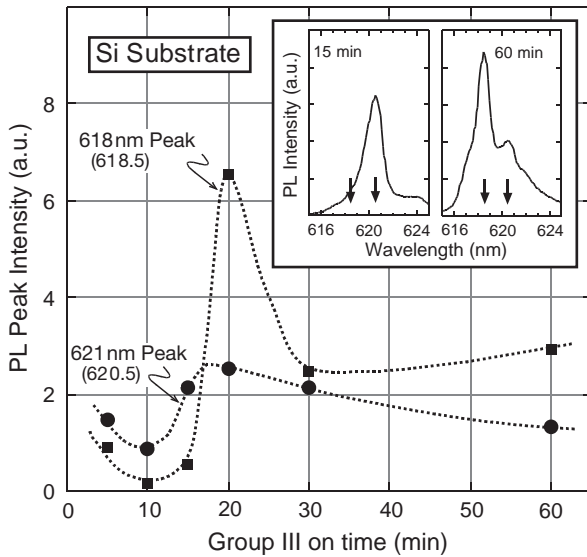


Fig. 3. Peak PL intensity at 621 and 618 nm against various IGE ON times on Si substrates. Inserts show the PL spectra from GaN:Eu samples with 15 and 60 min IGE ON times.

with group III cycling times. Rutherford back scattering experiments conducted on the GaN:Eu have previously concluded [17] that most of the  $\text{Eu}^{3+}$  ions are placed as substitutional impurities on Ga sites in the GaN host. At this time, it is not yet determined if the optically active  $\text{Eu}^{3+}$  ions are located substitutionally, interstitially, or some combination of both. However, based on the stronger PL and EL level generated under certain IGE conditions, it does appear that the IGE technique can result in a greater number of optically active  $\text{Eu}^{3+}$  ions within the GaN host than the conventional MBE technique. Further experiments are currently being conducted in order to gain a more detailed understanding of IGE-grown GaN:Eu material.

Careful examination of the PL spectra for different IGE GaN:Eu films on Si substrates shows an interesting transition in the intensity of the major red emission peak at different group III ON times. Fig. 3 illustrates the variation of the 618 and 621 nm peak intensities with IGE conditions. The accurate wavelengths for the peaks that we refer to as 618 and 621 nm are 618.5 and 620.5 nm, respectively. As also shown in the Fig. 3 inserts, at shorter IGE ON times (<15 min) the major Eu red emission is at 621 nm, whereas for longer (>20 min) IGE ON times the 618 nm peak is dominant. This shift of the dominant Eu emission from the 621 nm peak to the 618 nm peak with the increase in IGE cycling time can be attributed to changes in Eu incorporation (different concentration of various sites) in the host material structure due to the growth condition variations.

All GaN:Eu IGE films grown on both Si and glass substrates have strong red emission under PL excitation. Even though rare earth ions in GaN have narrow spectral emissions (for example the 621 nm Eu peak is  $\sim 3$  nm wide), the integrated peak intensity provides a better comparison of the strength of the PL emission. In order to calculate the integrated peak intensity for the 621 and 632 nm peaks, the PL peak was approximated by a Gaussian curve. The total emission for the 590–670 nm spectral ranges was integrated in a similar fashion. The

integrated PL intensity variation for 621 and 632 nm peaks and for all peaks in the entire red region (590–670 nm) with group III ON time are shown in Fig. 4 for GaN:Eu films grown on Si and on glass substrates. A clear pattern emerges with the 15–20 min IGE films producing the maximum increase in the PL intensity compared to the MBE film. In the case of GaN:Eu film grown on Si substrates, the maximum increase in the total red region PL intensity of  $\sim 3\times$  is obtained for the 20 min IGE film, while for glass substrates, the maximum increase of  $\sim 1.3\times$  is obtained for the 15 min IGE case.

The growth material can undergo both annealing and nitridation during the group V only period within each IGE cycle. To determine which of these two processes is more important for Eu emission we have compared the properties of three GaN:Eu samples grown by: (a) conventional MBE (60 min) only; (b) conventional MBE followed by in situ annealing; (c) conventional MBE followed by nitridation for 15 min at 800 °C. The Eu PL spectra of these three samples are shown in Fig. 5. A comparison shows that the effect of annealing on the Eu emission is negligible, whereas nitridation

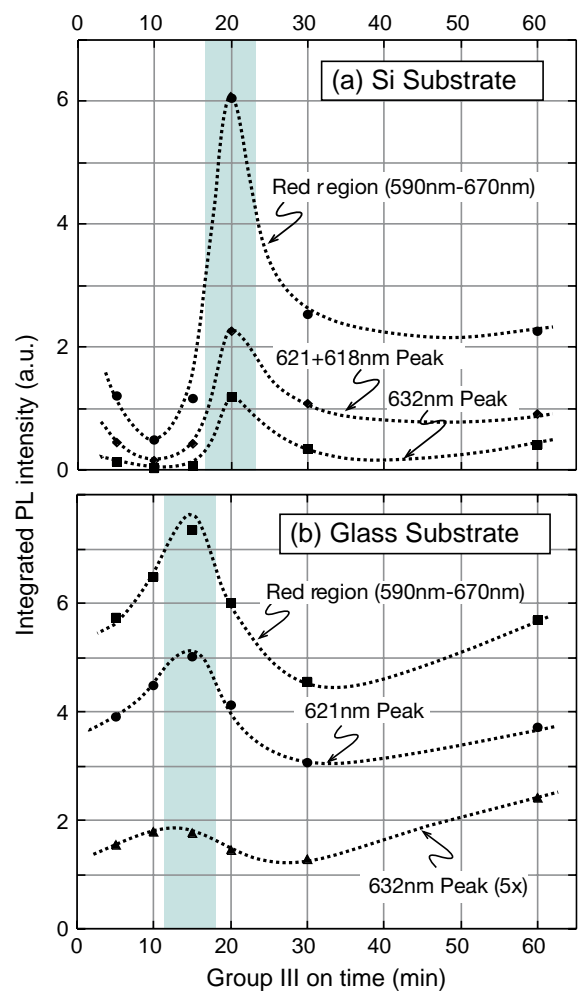


Fig. 4. Integrated PL intensity for 621 and 632 nm peaks, and for overall “red” (590–670 nm) emission. The highlighted regions show the optimum group III ON time on Si (a) and glass (b) substrates. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

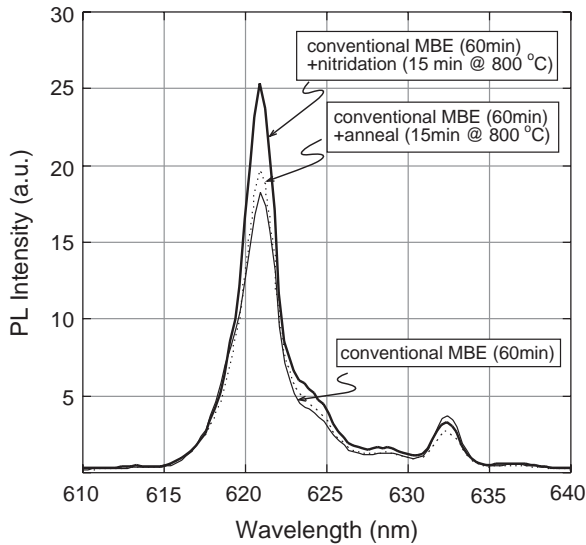


Fig. 5. PL intensity of GaN:Eu films grown by conventional MBE, conventional MBE+anneal (15 min at 800 °C); conventional MBE+nitridation (15 min at 800 °C). Film growth time was 60 min in all three cases.

results in a noticeable increase in intensity. This indicates that the dominant mechanism during the group V only time in IGE growth is nitridation rather than annealing. The PL enhancement after nitridation supports the hypothesis that there is insufficient amount of nitrogen incorporation in the GaN film during conventional MBE growth.

#### 4. TDEL device fabrication and measurements

We have utilized the IGE technique to improve the performance of GaN:RE EL phosphor in TDEL devices. The TDEL device structure was selected over the standard TFEL structure because of its very high device stability and inexpensive processing methods that do not require stringent fabrication techniques.

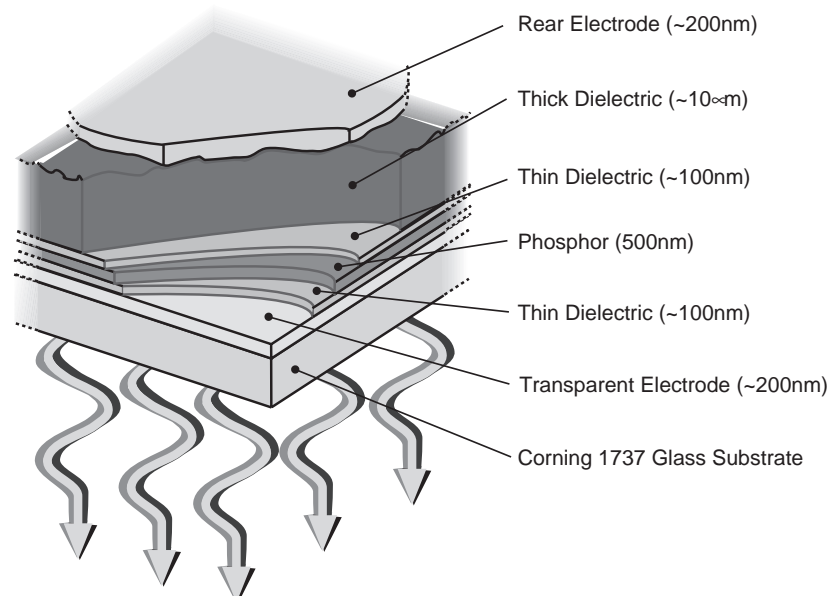


Fig. 6. GaN:Eu TDEL device structure.

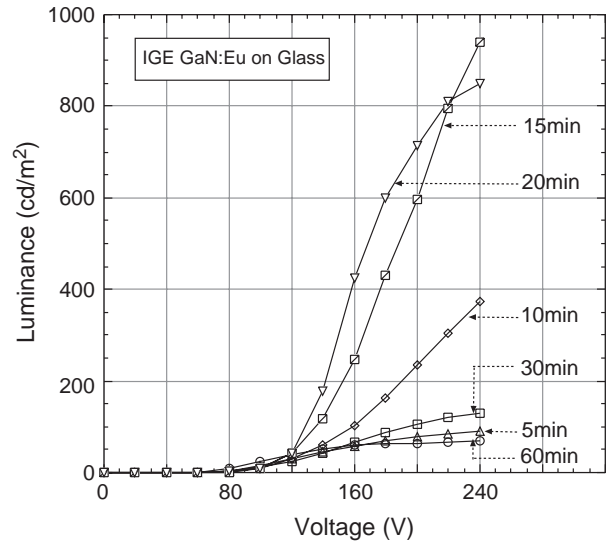


Fig. 7. Luminance vs. voltage for TDEL devices using IGE films grown at various ON times.

TDEL devices consisting of a metal-insulator-semiconductor-insulator-metal (MISIM) structure were fabricated on glass substrates as shown in Fig. 6. Sputtered indium tin oxide (ITO) films ( $\sim 200$  nm,  $< 20 \Omega/\square$ ) were used as the transparent metal contact from the viewing side of the TDEL while aluminum ( $\sim 200$  nm) was used for the opaque metal contact on the other end of the MISIM stack. Sputtered barium titanate (BTO,  $\epsilon_r \sim 20$ ) thin films ( $\sim 100$  nm) were used as insulator layers to encapsulate the GaN:Eu phosphor layer ( $\sim 500$  nm). The thin dielectric films act as charge trapping layers in the EL device. The thick dielectric layer was a lead zirconate titanate (PZT,  $\epsilon_r \sim 1000$ ) composite. We have observed that the PZT layer couples high charge densities across the phosphor while inhibiting catastrophic device failure. High charge density is desired to achieve a high luminance from the device, since photons are generated by hot electron impact excitation of

lumophores in the phosphor. The PZT thick dielectric layer has a thickness of  $\sim 10 \mu\text{m}$  resulting in a capacitance of  $\sim 80 \text{ nF/cm}^2$ . In general, there is a trade-off in most dielectric materials between the dielectric constant and the dielectric breakdown field. The PZT fabrication process has been modified in order to provide the highest dielectric constant consistent with a breakdown field ( $>0.3 \text{ MV/cm}$ ) high enough to allow efficient device performance. Detailed description on the TDEL device fabrication, device physics and characterization can be found in references [5,6,15].

Fig. 7 shows the luminance of GaN:Eu TDEL devices as a function of voltage for each group III ON time growth cycle. The devices were driven using a 1 kHz bipolar square waveform. The conventional MBE device corresponds to 60 min ON time. The strongest device luminance of nearly  $\sim 1000 \text{ cd/m}^2$  is observed for GaN:Eu layers with 15–20 min group III ON time, representing a  $\sim 10\times$  increase over devices fabricated using conventional MBE grown material.

The device luminance at several constant voltage levels ranging from 80 to 240 V is shown in Fig. 8 for various group III ON times. With the exception of the 80 V case, a similar trend is observed with maximum luminance for all voltage levels being around the 15–20 min group III ON time. The maximum luminance intensity level increase achieved through IGE growth technique is  $\sim 12\times$  that of conventional MBE GaN:Eu devices. The 80 V (close to the device turn-on voltage) luminance intensity curve also provides some valuable information on the IGE phosphor material. Ideally, at pre-threshold voltages the phosphor layer acts as a capacitor. In reality, however, the phosphor material always experiences some charge leakage at pre-threshold voltages. The presence of leakage charge can cause observable luminance at voltages below turn-on and a rather shallow rise in the luminance at modulation voltages above turn-on. The pre-threshold luminance hinders the high contrast that is desired in flat panel displays. In the 80 V curve in Fig. 8 we can see that the luminance around threshold in the optimized IGE GaN:Eu

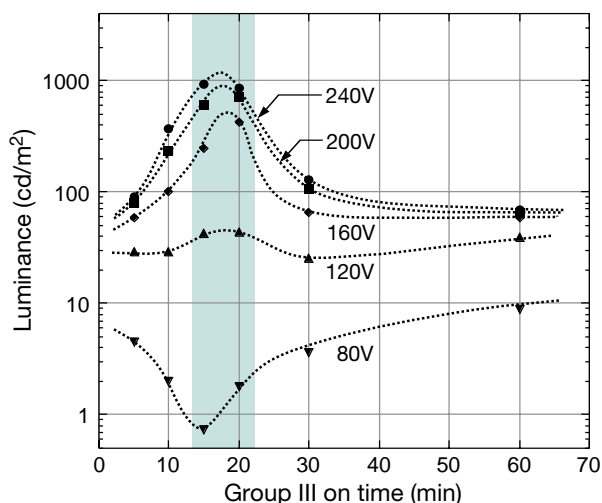


Fig. 8. TDEL device luminance measured at several fixed voltages for different group III ON times. The TDEL devices were driven using bipolar square waveform at 1 kHz.

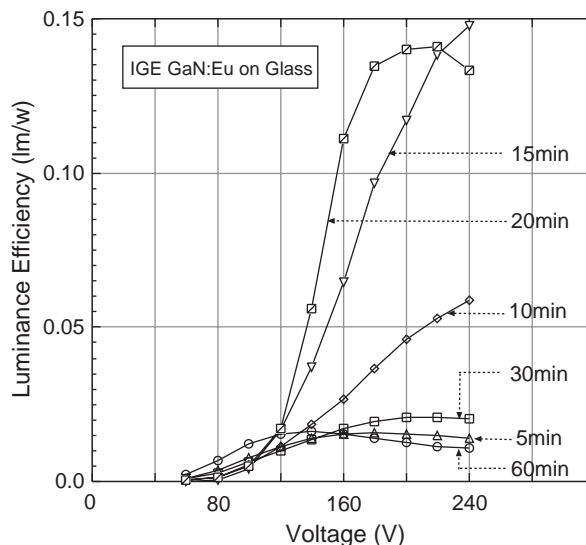


Fig. 9. TDEL device efficiency vs. voltage using IGE films grown at various ON times.

samples (15–20 min ON time) is almost  $10\times$  less than that of the conventional MBE GaN:Eu device. Combined with  $10\times$  increase in luminance above threshold, the luminance contrast for the 15–20 min IGE devices is  $100\times$  higher than that of the conventional MBE devices.

The luminance-voltage slope for the optimum IGE devices is much steeper than in the MBE device. The sharper luminance increase with increasing voltage is due to the increase in luminance efficiency. Possible reasons for increased device efficiency in the IGE process are the improvements made in the hot electron transport qualities of GaN:Eu [18]. For display applications, it is very important to have a high luminous efficiency as possible in the EL device in order to reduce the power consumption. The luminous efficiency of the GaN:Eu TDEL devices is shown in Fig. 9 as a function of voltage. The maximum luminous efficiency level reached at 240 V is  $\sim 0.15 \text{ lm/W}$  for the 15 min group III ON time devices. This is a factor  $\sim 15\times$  higher than that of the conventional MBE device. Even though theoretically a saturation and a reduction of the efficiency should be observed at higher voltages we only observe a saturation in the IGE GaN:Eu EL devices. The increase in the capacitance values within the dielectric films has led to a much larger power coupling across the phosphor layer. The higher power coupling is causing the lower levels of the luminous efficiencies even at high luminance levels of  $\sim 1000 \text{ cd/m}^2$ . The general trends shown by the luminous efficiency in Fig. 9 are similar to those shown by the luminous intensity in Fig. 7.

## 5. Conclusions

In conclusion, the interrupted growth epitaxy technique has demonstrated a significant improvement in the GaN:RE TDEL devices. Devices grown with 15–20 min IGE cycles have produced a  $\sim 15\times$  improvement in EL luminance over conventional MBE phosphors reaching  $\sim 1000 \text{ cd/m}^2$ . In addition, the IGE technique results in improvement of the

phosphor quality, leading to a  $\sim 10\times$  reduction in pre-threshold charge leakage. The luminous efficiency achieved by the 15–20 min IGE devices reached a maximum of  $\sim 0.15$  lm/W, which is  $>12\times$  that of the conventional MBE GaN:Eu EL devices. These advances in GaN:Eu TDEL devices make IGE a very attractive technique for phosphor material growth. The PL and EL measurements of IGE films and devices with various group III cycling indicate that the 15–20 min *ON* times provide the optimum conditions for the GaN:Eu on Si and glass substrates.

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