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Effect of growth conditions on Eu^{3+} luminescence in GaN

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ABSTRACT

Eu-doped GaN thin films were *in situ* grown on sapphire substrates by RF plasma-assisted solid-source molecular beam epitaxy technique. Strong red emission at ~622 nm from $^5D_0$–$^7F_2$ radiative transitions in Eu^{3+} ions was observed for all samples. The effects of important growth parameters, such as III/V ratio (Ga flux), Eu cell temperature (Eu flux) and growth temperature, on Eu^{3+} photoluminescence were studied. X-ray diffraction and secondary ion mass spectroscopy measurements were performed to investigate thin film quality and Eu doping profiles. The strongest Eu^{3+} luminescence was obtained from GaN:Eu thin films grown under slightly N-rich condition (III/V$<$1), while the highest Eu^{3+} emission efficiency was obtained in thin films grown under Ga-rich condition (III/V$\geq$1). The optimum Eu doping concentration for Eu^{3+} luminescence is ~(0.1–1.0) at% for III/V$\leq$1 ratio condition. Higher growth temperature ($>$750 °C) was also found to enhance Eu^{3+} luminescence intensity and efficiency.

1. Introduction

III-nitride semiconductors are widely researched for optoelectronic and photonic applications because their direct and wide energy bandgap from 0.7 eV (InN) to 6.2 eV (AlN) provides the potential for efficient emission from ultraviolet to infrared (IR). Violet, blue and green LEDs and lasers have been realized [1–4] by AlGaN and InGaN alloys. However, due to the degradation of InGaN crystal quality with high In mole composition, it is very difficult to realize efficient red light emission.

The rare earth (RE) element europium (Eu) is very attractive as a red light source because of its strong and sharp emission at ~622 nm, originating from $^5D_0$–$^7F_2$ radiative transitions of 4f–4f electrons in Eu^{3+} ions. GaN acts as an ideal host for RE elements because the wide energy bandgap enables low thermal quenching on RE emission and strong chemical bonding allows high RE doping. Red electroluminescence (EL) from Eu-doped GaN were realized with Schottky diode [5,6] structure on Si and AC thin film electroluminescent (TFEL) [7] structure on Si and glass. Stimulated emission from Eu^{3+} ions was also observed [8] and the first optically-pumped red GaN:Eu lasers were fabricated [9] on Si substrates.

Although RE emission spectra are independent of the host materials, the emission intensity and efficiency are highly dependent on host quality and RE doping concentration. The effects of Er doping concentration [10], Ga flux [11] and growth temperature [12] on Er^{3+} visible and IR luminescence, and the effect of growth conditions [13,14] on Eu^{3+} stimulated emission were studied by Steckl et al. at Cincinnati. For Eu luminescence, only V/III ratio and Eu concentration was studied [15,16] on GaN:Eu grown by NH_3-based gas-source molecular beam epitaxy (GSMBE). The effect of growth conditions on Eu^{3+} luminescence has not been systematically studied to date. In this paper, we report the optimization of GaN:Eu thin film epitaxial growth by plasma-assisted N_2-based solid-source molecular beam epitaxy (SSMBE) technique based on the effect of fundamental growth parameters, such as III/V ratio, Eu cell temperature and growth temperature.

2. Experiment details

All Eu-doped GaN thin films were grown on C(0 0 0 1) sapphire substrates in a Riber 32 SSMBE system. 6 N Ga and 3 N Eu metal were evaporated in conventional solid Knudsen effusion sources. Ultrahigh pure N_2 gas was introduced by a mass flow controller and discharged into the plasma by a 13.33 MHz RF generator. After wet chemical cleaning and high vacuum degassing (~500 °C), the sapphire wafers were nitridated in N_2 plasma only at 850 °C for 10 min prior to the growth. A 20 nm GaN buffer layer was grown at low temperature (~500 °C), followed by Eu-doped GaN layer growth for 1 h. Several sets of Eu-doped GaN thin films were grown with different growth conditions.

Characterization of GaN:Eu thin films was carried out by photoluminescence (PL), X-ray diffraction (XRD) and secondary ion mass spectroscopy (SIMS) measurements. Eu^{3+} PL emission

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was excited "above-bandgap" by a 325 nm He–Cd laser. The spectra were acquired by a high-resolution spectrometer equipped with a PMT detector. XRD measurements were performed with a Cu Kα X-ray gun at 1.542 Å to check the crystallographic quality of GaN:Eu thin films. Eu doping profiles were investigated by a PHI D-SIMS 6600 system with an oxygen beam and Eu atomic concentrations were estimated.

3. Results and discussions

3.1. Effect of III/V ratio

Since Ga and N are introduced independently in MBE growth, the III/V (Ga/N) ratio plays an important role during the growth process. In RF plasma-assisted SSMBE system, the N_2 plasma typically consists of ~5% N atoms and ~95% N_2 molecules with a pressure of $\sim 10^{-5}$ Torr. Because the plasma is affected by the gas flow rate, RF power and the system pressure, it is not easy to precisely control the N flux. On the other hand, the Ga flux is exponentially proportional to the Ga cell temperature, which can be easily measured as beam equivalent pressure (BEP) by an ion gauge. Therefore, the Ga cell temperature was varied to produce different III/V ratio growth conditions.

A set of Eu-doped GaN samples were grown on sapphire substrates with different III/V ratios. The N_2 gas flow was maintained at 2.2 sccm and the plasma was generated under 400 W RF power in the chamber with the system pressure of $\sim 5.5 \times 10^{-5}$ Torr. The growth temperature was set at 800 °C and the Eu cell temperature was set at 450 °C. The Ga cell temperature was varied from 810 to 910 °C with steps of 20 °C, corresponding to Ga flux ranging from 0.9×10^{-7} to 8.4×10^{-7} Torr. The growth rate of GaN:Eu thin films is plotted versus Ga flux and Ga cell temperature in Fig. 1. Initially, the growth rate increased monotonically with Ga flux, but after reaching $\sim(3.5–4.0) \times 10^{-7}$ Torr it remained constant at ~500 nm/h. The shaded column in Fig. 1 indicated the range of stoichiometric growth conditions, where III/V ratio equals ~1.0. The left side is the N-rich condition (III/V < 1), where the growth rate was limited by Ga flux; the right side is the Ga-rich condition (III/V > 1) where the growth rate was saturated due to the limitation of N flux.

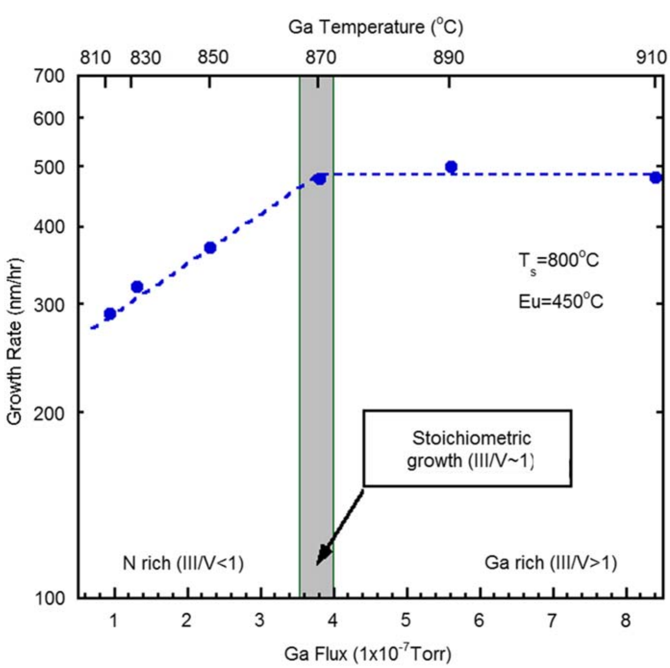

Fig. 1. (Color on-line) Growth rate of GaN:Eu thin films grown on sapphire wafers by SSMBE technique. (Shaded column shows stoichiometric growth condition range: III/V~1.)

The crystallographic quality of GaN:Eu thin films was investigated by XRD measurements. A typical result from the GaN:Eu film grown on sapphire is shown in Fig. 2a. There is a strong peak at ~34.6°, corresponding to the α-GaN(0 0 2) orientation. Generally, high peak intensity and narrow peak width indicated thin film of high quality. Fig. 2b shows the intensity and FWHM of the GaN(0 0 2) peak as a function of Ga flux. Good quality GaN thin films were generally obtained under Ga-rich conditions. The stoichiometric condition range (shaded column in the figure) acts as a very clear border between high- and low-quality GaN:Eu thin films. The Eu doping profile was measured by SIMS system and Fig. 3a shows typical measurement from GaN:Eu thin films. The Eu atomic concentrations in film grown with different III/V ratios (i.e. at different Ga flux levels) are plotted in Fig. 3b. With increasing Ga flux, the Eu atomic concentrations decreased hundred-fold from ~2.0 at% down to

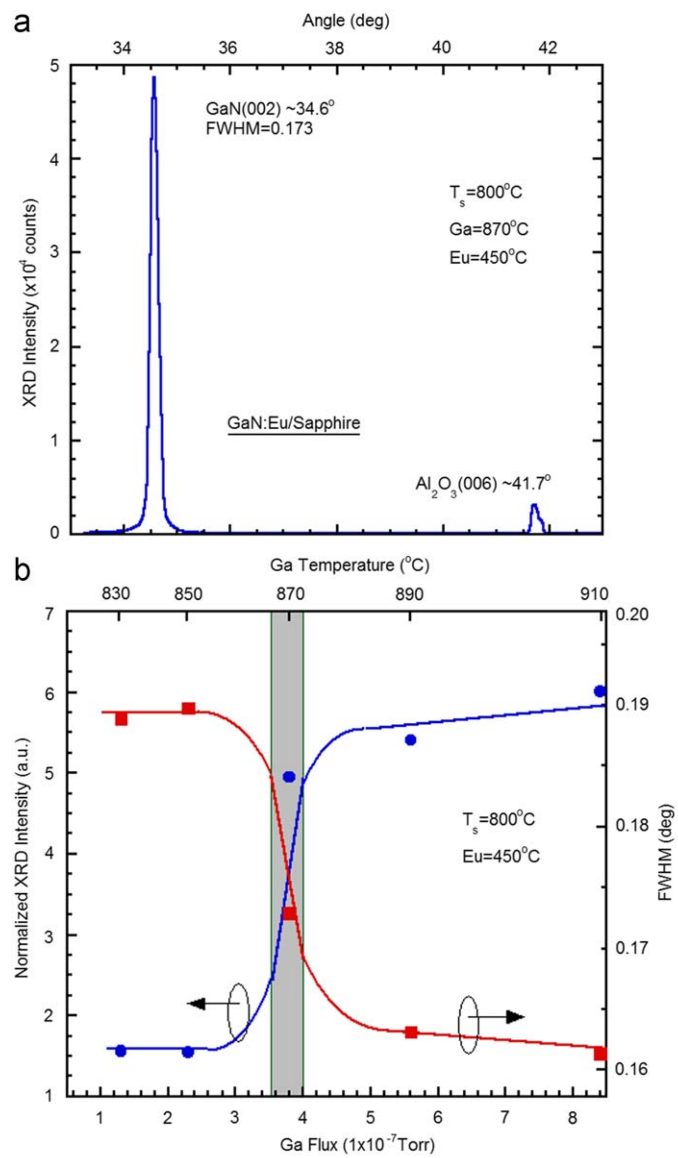

Fig. 2. (Color on-line) Structural characteristics of GaN:Eu thin films investigated by X-ray diffraction (XRD) measurements: (a) typical XRD result from GaN:Eu/sapphire sample and (b) GaN(0 0 2) peak intensity and FWHM dependence on III/V ratio condition.

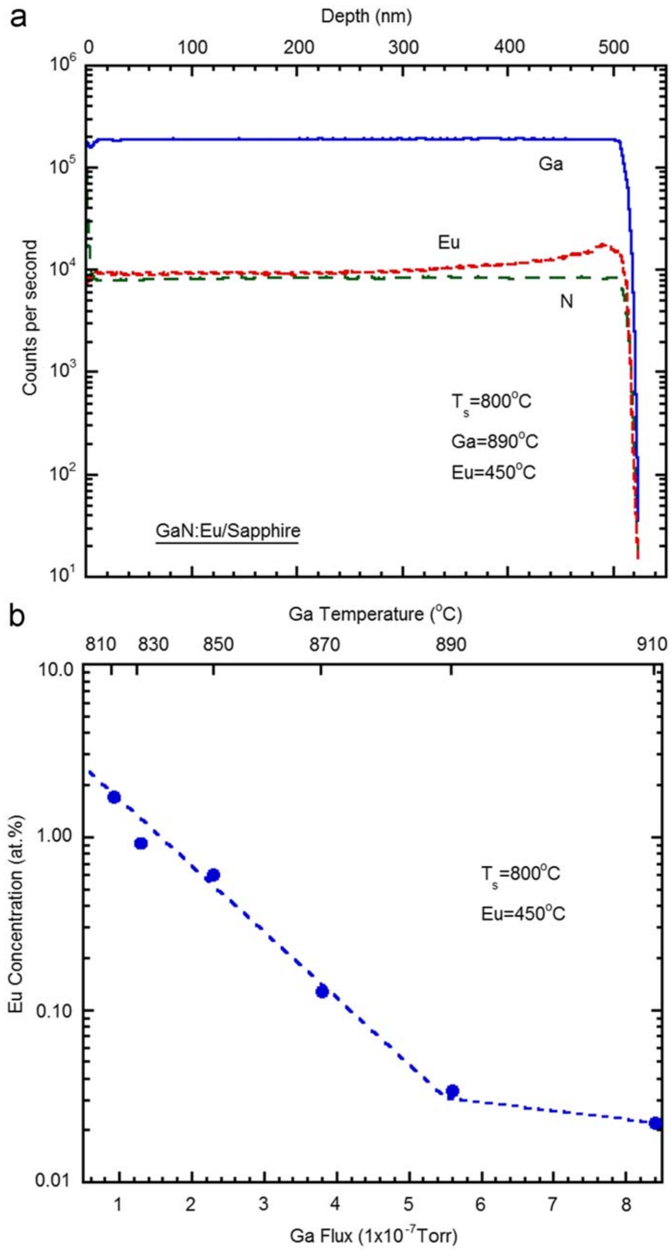

Fig. 3. (Color on-line) Eu doping profile in GaN:Eu thin film measured by secondary ion mass spectroscopy (SIMS) system: (a) typical SIMS result from GaN:Eu/sapphire sample and (b) estimated Eu atomic concentration plotted versus Ga flux.

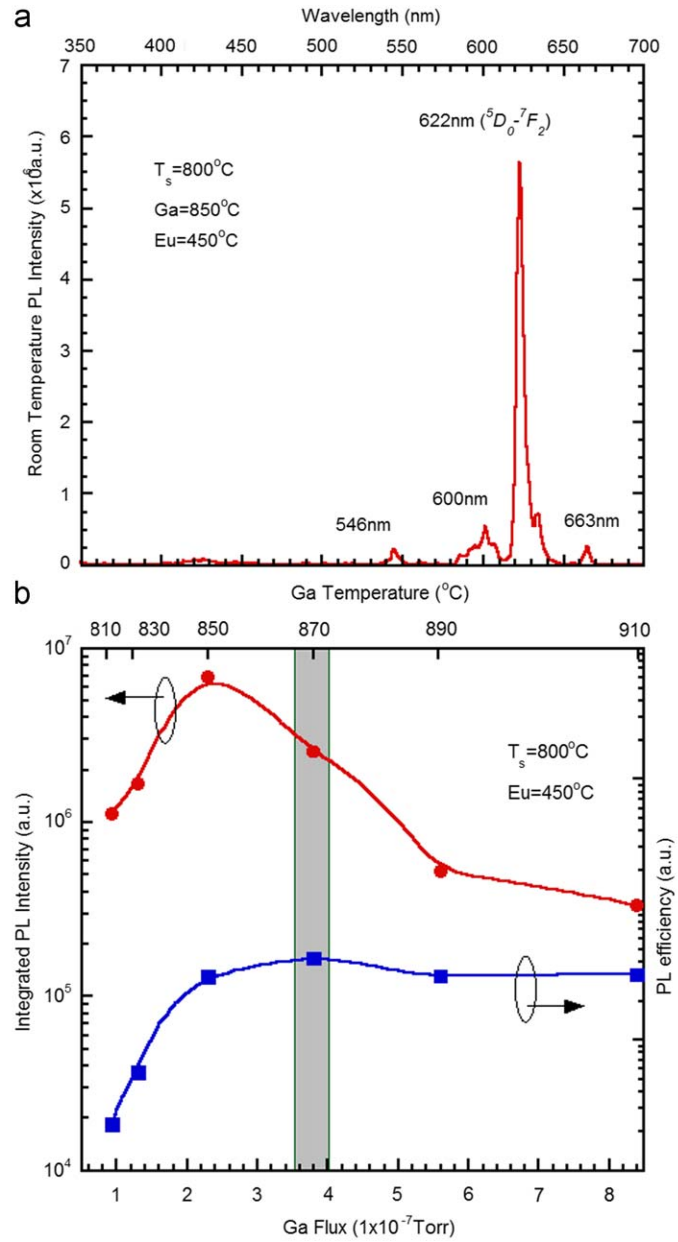

Fig. 4. (Color on-line) Eu^{3+} red emission studied by room temperature photoluminescence (PL) measurements: (a) typical PL spectra from GaN:Eu/sapphire sample and (b) Eu^{3+} PL intensity and efficiency dependence on Ga flux (PL efficiency calculated as raw intensity divided by Eu atomic concentration and film thickness).

~0.02 at%. At lower Ga flux, larger numbers of Eu atoms could be incorporated due to the lower growth rate of GaN:Eu thin films. At higher Ga flux, the site competition between Ga and Eu atoms decreased the Eu concentration.

Eu^{3+} luminescence was investigated by room temperature PL measurement. A typical PL spectrum is shown in Fig. 4a. The main peak at ~622 nm is produced by radiative transitions of $^5D_0$–$^7F_2$ energy levels. There are also several minor peaks at ~600 nm ($^5D_0$–$^7F_1$), ~663 nm ($^5D_0$–$^7F_3$) and ~546 nm ($^5D_1$–$^7F_1$) from Eu^{3+} ions. In order to study the effect of III/V ratio, the PL intensity was integrated over the main peak (~622 nm) and plotted as the red curve in Fig. 4b. The strongest PL emission was obtained from GaN:Eu thin films under slightly N-rich condition, where overall thin film quality is not optimum. Since Eu atomic concentration in GaN thin films decreased with Ga flux (seen in Fig. 3), it is appropriate to calculate the Eu^{3+} PL efficiency (raw PL intensity divided by Eu atomic concentration and film thickness). The results are plotted as the blue curve in Fig. 4b. The PL efficiency increases with Ga flux under N-rich condition and becomes almost constant in the III/V $\geq$ 1 region.

3.2. Eu cell temperature

The above results showed that high-quality GaN:Eu thin films have better emission efficiency, but low emission intensity mainly due to low Eu concentration. And the most direct method to increase Eu concentration is to increase the Eu flux. However, it is well known that RE luminescence suffers from a concentration quenching effect [17] in the host. This effect is caused by energy migration or cross relaxation process between neighboring RE ions, resulting in an increase in the nonradiative relaxation. Therefore, it is important to optimize Eu doping concentration. Since Eu flux and Ga flux both affected the Eu incorporation, three sets of samples were grown with different Eu cell temperature under different III/V ratio condition: slightly N-rich condition (III/V $<$ 1), stoichiometric condition (III/V$\sim$1) and slightly Ga-rich condition (III/V $>$ 1). The growth temperature was kept at 800 °C and the nitrogen gas flow was kept 2.2 sccm. The Eu cell temperature was varied from 430 to 490 °C for each set.

The Eu atomic concentration of all samples was determined from SIMS measurements and the results are plotted in Fig. 5. The Eu concentration increases almost exponentially with Eu cell temperature for all three sets, while higher Ga flux results in lower Eu incorporation in GaN thin films. XRD measurement results shows that III/V$\geq$1 ratio produces high-quality GaN:Eu thin films, consistent with the results shown in Fig. 2b (not shown here). The corresponding PL intensity integrated over the main peak at $\sim$622 nm is plotted versus Eu atomic concentration in Fig. 6. It clearly shows that the strongest PL intensity occurs at different Eu concentrations for different III/V ratios. One can divide the Eu atomic concentration into several ranges in Fig. 6. In range (i) for Eu atomic concentration below $\sim$0.034 at%, Eu^{3+} PL intensity is very low due to very low Eu concentration. When Eu concentration is in range (ii) of $\sim$(0.034–0.2) at%, GaN:Eu thin films grown under stoichiometric condition (III/V$\sim$1) have the highest Eu^{3+} PL intensity and fair GaN:Eu quality, which is very promising for the application of GaN:Eu LEDs and lasers. With Eu concentration increasing from $\sim$0.2 to 2.0 at% in range (iii), Eu^{3+} PL from low quality of GaN:Eu thin films have the strongest PL intensity due to the defect-mediated mechanism [18,19]. The decrease of Eu^{3+} PL from high quality of GaN:Eu thin film grown under III/V$\geq$1 condition is possibly related to the high Eu and Ga fluxes inducing the formation of Eu clusters, resulting in concentration quenching effects. After Eu concentration reaches over 2.0 at% in range (iv), a sharp decrease of Eu^{3+} PL intensity occurs, probably due to a strong concentration quenching effect. The optimum Eu doping concentration appears to be $\sim$(0.1–1.0) at% with III/V$\leq$1 ratio condition, shown as the range within in the oval in Fig. 6.

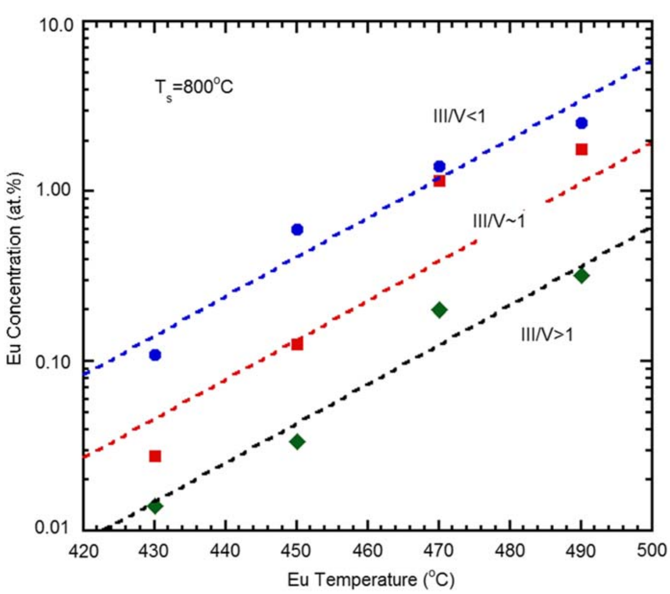

Fig. 5. (Color on-line) Eu atomic concentration plotted versus Eu cell temperature, higher III/V ratio condition resulted in lower Eu doping concentration.

3.3. Growth temperature

Another basic growth parameter is the substrate temperature. A set of GaN:Eu samples were grown on sapphire at different growth temperatures from 600 to 900 °C. N_2 plasma was generated under 400 W RF power at a flow rate of 2.2 sccm. Ga and Eu cell temperatures were kept at 870 and 450 °C for all samples. Since the range of growth temperature is not very large, all growths are still considered in the stoichiometric condition range (III/V$\sim$1).

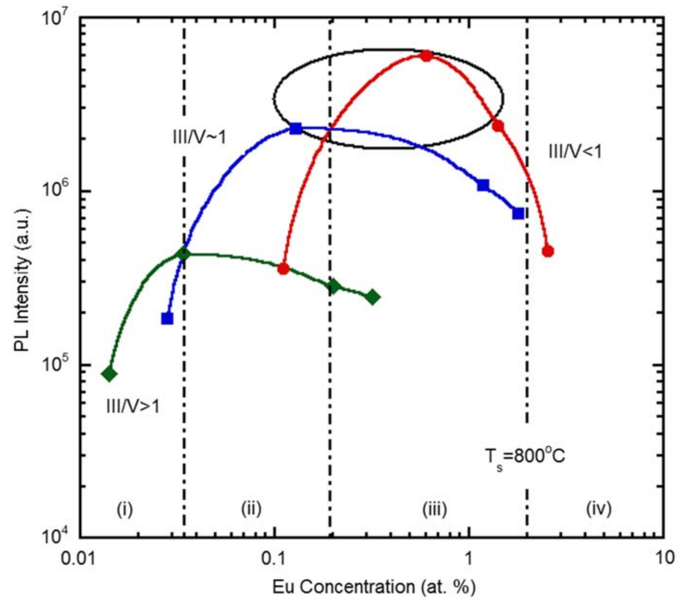

Fig. 6. (Color on-line) Eu^{3+} PL intensity dependence on Eu atomic concentration and III/V ratio condition, optimized Eu doping concentration range shown in oval shape (0.1–1.0 at%).

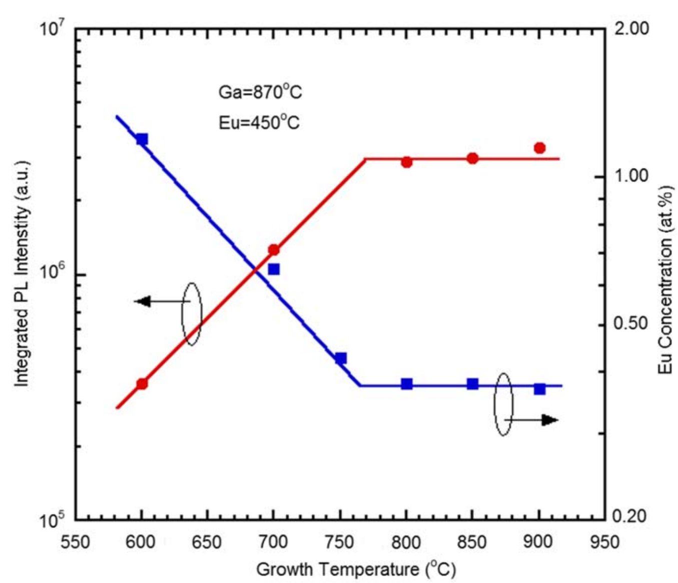

Fig. 7. (Color on-line) Eu atomic concentration and Eu^{3+} PL intensity plotted versus growth temperature.

The Eu atomic concentration as a function of growth temperature was obtained from SIMS measurements and is shown in Fig. 7. The Eu concentration is $\sim$1.2 at% for growth temperature at 600 °C, and reached $\sim$0.37 at% for $\geq$750 °C growth. Room temperature PL measurements were performed on these samples and the results are also shown in Fig. 7. With growth temperature increasing, Eu^{3+} PL intensity increases monotonically until reaching saturation level after $\sim$750 °C, which is a complementary trend of the Eu doping concentration. It is apparent that higher growth temperature ($\geq$750 °C) enhanced Eu^{3+} PL intensity $\sim 10\times$, while reducing the Eu atomic concentration $\sim 3\times$. An enhancement of $\sim 30\times$ on Eu^{3+} PL efficiency was reached.

4. Conclusions

Eu-doped GaN thin films were successfully grown by RF plasma-assisted SSMBE technique. Strong red emission was obtained at $\sim$622 nm from Eu^{3+} ions, but the emission intensity and efficiency are highly dependent on the growth conditions. It was found that the strongest Eu^{3+} luminescence was obtained from GaN:Eu thin films grown under slightly N-rich condition, while the highest Eu^{3+} emission efficiency was from high-quality thin films grown under Ga-rich condition. The optimum Eu doping concentration for Eu^{3+} PL intensity is $\sim$(0.1–1.0) at% for III/V <1 condition. Higher growth temperature ($\geq 750^{\circ}$ C) can also enhance Eu^{3+} emission efficiency and intensity.

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