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## Enhanced photo/electroluminescence properties of Eu-doped GaN through optimization of the growth temperature and Eu related defect environment

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The influence of growth temperature on the surface morphology and luminescence properties of Eu-doped GaN layers grown by organometallic vapor phase epitaxy was investigated. By using a Eu source that does not contain oxygen in its molecular structure, and varying the growth temperature, the local defect environment around the Eu<sup>3+</sup> ions was manipulated, yielding a higher emission intensity from the Eu<sup>3+</sup> ions and a smoother sample surface. The optimal growth temperature was determined to be 960 °C and was used to fabricate a GaN-based red light-emitting diode with a significantly higher output power. © 2016 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>). [<http://dx.doi.org/10.1063/1.4950826>]

III-nitride materials have been given considerable attention in order to achieve efficient high intensity visible light emitters. Although blue and green light-emitting diodes (LEDs) have already been commercialized, nitride-based red and infrared LEDs are still at a premature stage of development. Since the indium composition of InGa<sub>N</sub> is limited by its low miscibility, the growth of InGa<sub>N</sub> layers with high In composition and good crystalline quality remains a challenge.<sup>1</sup> Recently, a red LED based on In<sub>x</sub>Ga<sub>1-x</sub>N/GaN multiple quantum well (MQW) has been developed;<sup>2-4</sup> however, a special reactor design was needed and the full width at half maximum (FWHM) increased during increased current injection. On the other hand, there have been several reports on the properties of Eu-doped GaN (GaN:Eu) based red LEDs in recent years.<sup>5-7</sup> These LEDs can be grown using the conventional organometallic vapor-phase epitaxy (OMVPE) method, and the FWHM of the emission is <1 nm. These properties make it possible to manufacture blue, green, and red LEDs on a single substrate. Several improvements have led to a maximum output power of 93 μW with an injection current of 20 mA;<sup>8</sup> however, further improvement can be attained by studying and optimizing the optical properties of the GaN:Eu active layers.

As many as eight incorporation centers have been identified in GaN:Eu grown by OMVPE.<sup>9</sup> However, it has been determined that two of these centers, referred to as OMVPE4 and OMVPE7, are of primary importance. OMVPE4 is referred to as the majority center as it represents ~85% of the Eu incorporation. However, OMVPE7, which only represents ~4% of the Eu incorporation, is the dominant center under above bandgap excitation. This is due to its high energy transfer efficiency as a result of its favorable local defect environment.<sup>8</sup> In this regard, the importance of donors and acceptors local to the Eu ions for enhanced energy transfer has also been reported.<sup>10,11</sup> It was proposed that the energy transfer efficiency from the GaN host to both OMVPE4 and OMVPE7 can be enhanced by the presence of defects such as vacancies and O.<sup>12</sup> It appears that higher luminescence can be achieved by modifying the local defect environment of the Eu ions.

Recently, a novel organometallic Eu source that does not contain oxygen in its molecular structure (EuCp<sup>pm</sup><sub>2</sub>) was investigated.<sup>13</sup> Using this source, it was found that either additionally supplied



oxygen or a new growth structure was necessary to attain uniform Eu incorporation and luminescence properties comparable to samples grown with the commonly used Eu source,  $\text{Eu}(\text{DPM})_3$ .<sup>5–12</sup> Also, when additional oxygen was not supplied, it was found that ~30% of the Eu ions no longer occupied Ga sites, as is typical in GaN:Eu.<sup>13,14</sup>

Several studies have shown that the defect environment in GaN, such as the vacancy and impurities concentrations, can be modified by controlling growth temperature.<sup>15–17</sup> In this article, a new defect environment is achieved by utilizing  $\text{EuCp}^{\text{pm}}_2$  as the Eu source and adjusting the growth temperature, which led to a significant enhancement in the emission intensity of a GaN:Eu based red LED.

A series of GaN:Eu samples were fabricated using the OMVPE method. Trimethylgallium (TMGa) and ammonia ( $\text{NH}_3$ ) were used as starting sources, and  $\text{EuCp}^{\text{pm}}_2$  was used as the Eu source. The Eu source and transfer lines were maintained at 125 °C and 135 °C, respectively. An optical microscope (Olympus/BX51M) was used to evaluate the surface morphology, and photoluminescence (PL) was used to investigate the optical properties. The PL measurements were carried out by exciting the Eu ions both resonantly and indirectly via excitation of the GaN host. The Eu ions were excited indirectly using the 325 nm line of a He-Cd laser, and resonantly using a photoluminescence excitation/emission (PLE) mapping technique referred to as combined excitation-emission spectroscopy (CEES). Details about this technique can be found elsewhere.<sup>9,18</sup> Resonant excitation gives information on the local environments of the various Eu centers, while indirect excitation gives information on the ability of each Eu center to acquire energy from the GaN host, and is similar to the process by which Eu ions are excited during current injection.

Positron-annihilation spectroscopy (PAS) has been widely used to investigate the native defect profile of nitride semiconductors and rare-earth doped GaN that were grown with different conditions.<sup>19,20</sup> Since the samples in this study were also varied by changing the growth temperature, PAS measurements were performed to explore the resulting change in the defect profiles. An LED was also fabricated using the growth structure and procedure explained in detail in Ref. 6. The light output power of the LEDs was measured using an integrating sphere spectrometer (Labsphere/LMS-100).

The surface morphology of GaN:Eu grown at various temperatures is shown in Fig. 1. At a growth temperature of 1030 °C, the sample surface appears rough, and a precipitation is clearly visible (Fig. 1(a)). Using bright field transmission electron microscopy (TEM), a precipitation can be seen clearly surrounding the GaN. The TEM diffraction pattern in this view shows a combination of spots and rings, and it is well-known that single crystals form spot diffraction patterns. While a clear hexagonal shape can also be seen in Fig. 1(b), which means that the plane of GaN is c-plane, four rings can be also observed. These rings would be the expected result from a polycrystalline cubic crystal structure. As EuN has a cubic crystal structure, and the precipitations are polycrystalline, the diffraction pattern rings were considered to be from EuN. The cubic EuN lattice indexing from the observed rings was compared with the standard X-ray diffraction powder pattern database (NBS25-4). The database values for the lattice constant for the (111), (200), and (220) planes are 2.8948 Å, 2.5070 Å, and 1.7727 Å, respectively. The values determined for the precipitation in our samples were 2.8763 Å, 2.4892 Å, and 1.7662 Å, respectively. This agreement confirms that the precipitation is EuN.

When the growth temperature was lowered to <1000 °C, the surface became smoother and mirror-like; moreover, no precipitation could be observed in Figs. 1(c) and 1(d). The lack of precipitation indicates that growth at low temperature leads to an environment that is more suitable for stable Eu incorporation into the GaN host. This improved Eu incorporation should have a profound impact on the optical properties of the material, which was investigated using PL.

Figure 2 shows the PL emission spectra for samples grown at various temperatures, under indirect excitation. When the growth temperature was reduced to 960 °C, the integrated PL intensity increased nearly 2 times as compared to the sample growth at 1030 °C. Further reduction of the temperature to 900 °C resulted in a lower integrated PL intensity because compared to the 960 °C sample ( $\text{Eu} \sim 5.6 \times 10^{19} \text{ cm}^{-3}$ ), the 900 °C sample ( $\text{Eu} \sim 4.6 \times 10^{19} \text{ cm}^{-3}$ ) had a lower Eu ion concentration. Also, the GaN band edge emission from the 900 °C sample was considerably weaker than that from the 960 °C sample, which implies that there are significant non-radiative processes

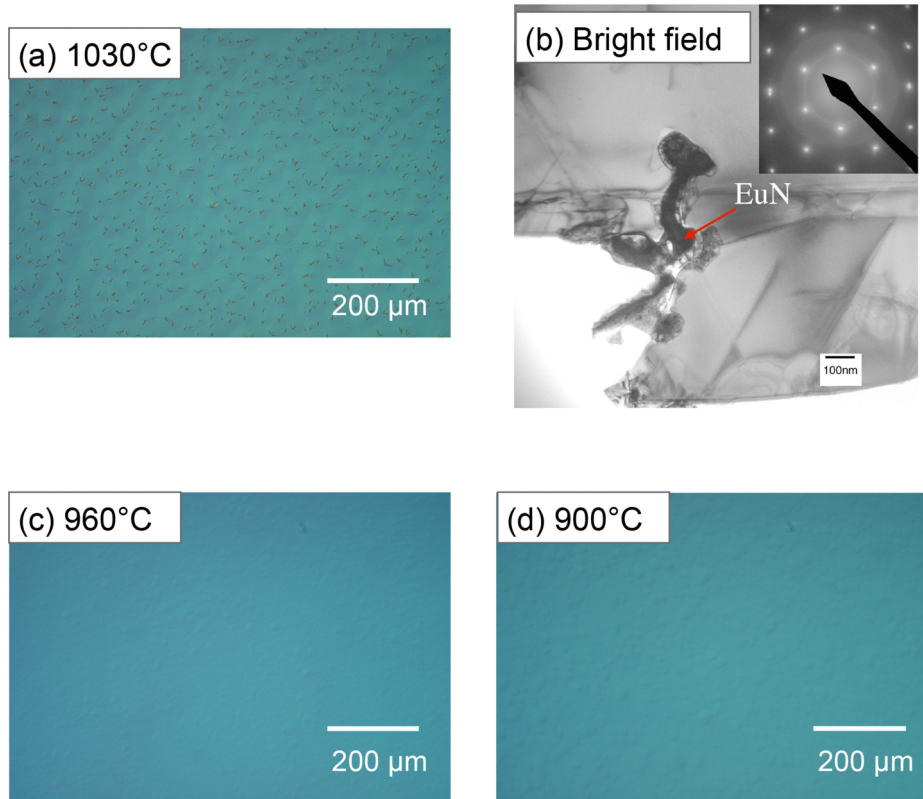


FIG. 1. Surface morphologies of samples grown at different temperatures. The sample grown at (a) 1030 °C has a rough surface, where the EuN precipitation forming polycrystalline can be observed by TEM and confirmed by TEM diffraction pattern in (b); (c) 960 °C has a smooth surface, where no precipitation can be observed; (d) 900 °C has a smooth surface as the 960 °C grown sample.

occurring, and that these are not influenced by the Eu excitation process. Moreover, the PL spectra of samples growth with  $\text{EuCp}^{\text{pm}}_2$  are typically quite broad, unless additional O is co-doped.<sup>13</sup> However, the PL spectra of the samples grown at lower temperatures were more resolved than the samples grown at 1030 °C.

To explore the impact of lowering the growth temperature on the defect environment of the Eu ions and their individual optical properties, the technique of CEES was utilized. The CEES results for the samples grown at 1030 °C and 960 °C (Fig. 3) show that the spectral shape of OMVPE4 was consistent in both samples. Conversely, the excitation/emission profile of OMVPE7 in the 960 °C sample exhibited fluorescence line narrowing. This indicates the existence of multiple small variations in local structure around OMVPE7. Each of these variations induces a slightly different perturbation on the localized crystal field of the “normal” OMVPE7, shifting its excitation and emission to different energies. Considering that OMVPE7 is the most prominent center contributing to both PL and EL emission, this change was beneficial and further investigation was necessary.

As it is believed that the appearance of multiple OMVPE7 centers results from slight variations in the local structure around the Eu ions, it is expected that a new defect environment has been created in the samples grown at low temperature as compared to those grown at 1030 °C. To explore the changes in the defect profiles for the various growth temperatures, PAS measurements were performed. In PAS measurements,  $S$ - and  $W$ -parameters are usually used to characterize the annihilation peak.<sup>19,20</sup> Here, the  $(S, W)$  values correspond to the annihilation of positrons in GaN:Eu which were measured by a coincidence-detection system. It is well known that by plotting  $S$  versus  $W$ , one can determine whether or not a defect type remains unchanged under external influence.<sup>19,20</sup> The  $(S, W)$  values obtained through the first-principle calculations are shown as blue symbols in Fig. 4, where the calculation was performed for the annihilation of positrons from the delocalized

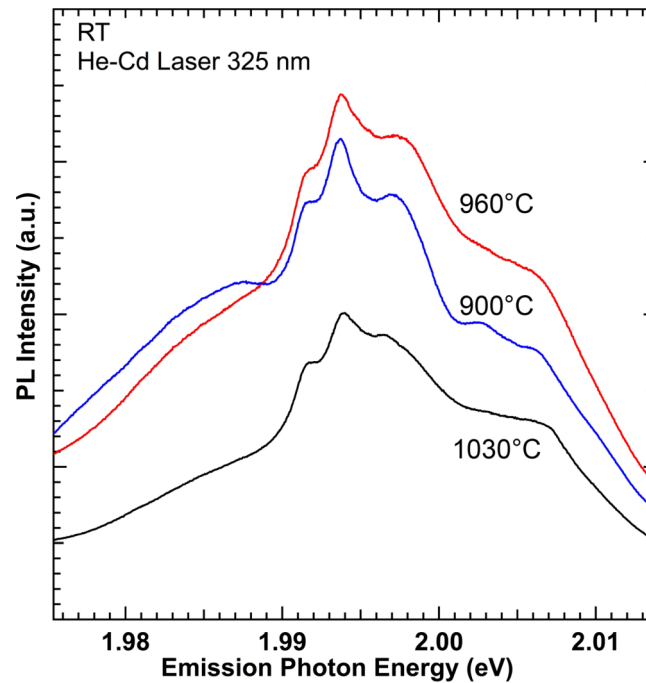


FIG. 2. Room-temperature PL spectra of samples grown at different temperatures: (1) 1030 °C has the weakest PL intensity because a significant number of the Eu ions have precipitated out as EuN; (2) 960 °C—the integrated PL intensity nearly doubles as compared to the sample grown at 1030 °C; (3) further reduction of growth temperature to 900 °C resulted in an integrated PL intensity which was lower compared to 960 °C growth, but higher than 1030 °C.

state (defect free) and for the annihilation of positrons trapped by gallium vacancies ( $V_{\text{Ga}}$ ), and  $V_{\text{Ga}}$  complex, such as  $V_{\text{Ga}}\text{-O}$  and  $V_{\text{Ga}}\text{-V}_\text{N}$ .<sup>19,20</sup>

The ( $S$ ,  $W$ ) values of different growth temperature samples were shown as black symbols in Fig. 4. For the sample grown at 1030 °C, the ( $S$ ,  $W$ ) value was located on the straight line connecting the values for defect free (DF) and gallium vacancy ( $V_{\text{Ga}}$ ) calculations. When Eu was doped into samples grown at 900 °C and 960 °C, the ( $S$ ,  $W$ ) values of these samples shifted to the left along the trend line towards that of a  $V_{\text{Ga}}$  coupled with four oxygen atoms [ $V_{\text{Ga}}\text{O}_4$ ], suggesting that number of oxygen coupling with  $V_{\text{Ga}}$  increased with decreasing growth temperature. Based upon those results, it is inferred that for the lower growth temperatures, the average local environments of the

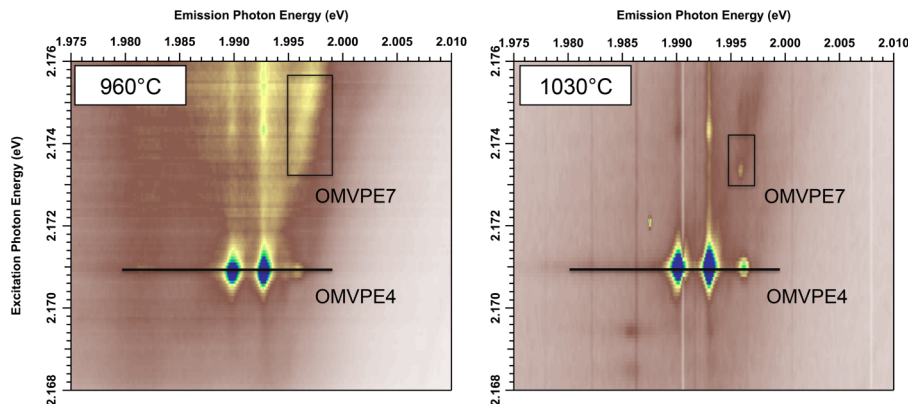


FIG. 3. CEES map of samples grown at 960 °C and 1030 °C. The spectral shape of OMVPE4 was consistent in both samples. Conversely, the excitation/emission profile of OMVPE7 in the 960 °C sample exhibited fluorescence line narrowing. This indicates the existence of multiple small variations in local structure around OMVPE7 that each induces a slightly different perturbation of the localized crystal field of the “normal” OMVPE7, shifting its excitation and emission to different energies.



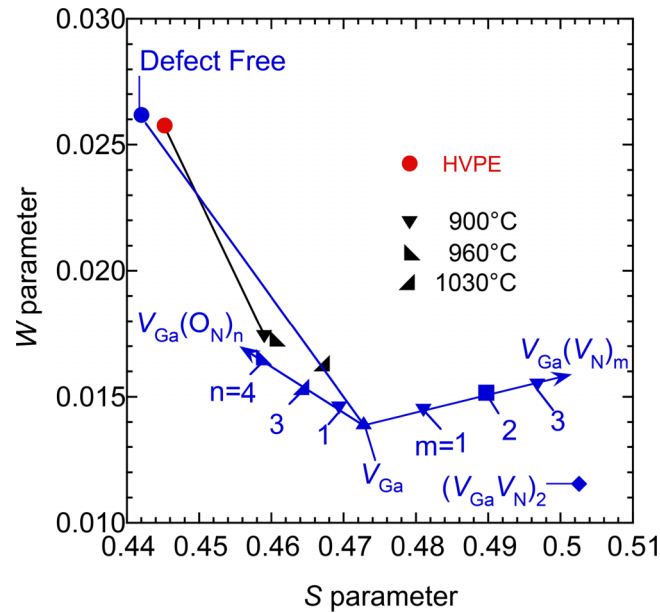


FIG. 4. The  $(S, W)$  values corresponding to the annihilation of positrons in GaN:Eu with growth temperatures of 1030 °C, 960 °C, and 900 °C are indicated by black symbols. The HVPE data come from a standard sample used to calibrate the PAS measurement. The  $(S, W)$  values, as calculated using the first principles, are indicated by blue symbols. The locations of measured  $(S, W)$  values suggest that the concentration of gallium vacancies ( $V_{\text{Ga}}$ ) decreases as the growth temperature is reduced. However, it was also observed that the samples grown at 960 °C and 900 °C are located close together, and just off of the straight line connecting the defect free (DF) value to the  $V_{\text{Ga}}$  value, which is different from the sample grown at 1030 °C. This indicates that, for growth at 960 °C and 900 °C, the average local environment of the remaining  $V_{\text{Ga}}$  contains two or more oxygen, while the  $V_{\text{Ga}}$  in the sample grown at 1030 °C would only have one or none at all.

remaining  $V_{\text{Ga}}$  have two or more oxygen in its close vicinity. On the other hand, for the sample grown at 1030 °C, the local environment of  $V_{\text{Ga}}$  would have only one or no oxygen at all.

It was previously reported that for samples grown at 1030 °C with  $\text{EuCp}^{\text{DPM}}_2$  as the Eu precursor, it was necessary to co-dope the sample with additional oxygen in order to reduce surface precipitation and attain more resolved PL spectra.<sup>13</sup> Therefore, it appears that lowering the growth temperature produces a growth environment where more of the oxygen that is normally introduced during the OMVPE growth of all GaN is incorporated. This growth condition also facilitates the formation of new  $V_{\text{Ga}}\text{-O}_N$  complexes. It has been suggested that OMVPE7 contains a  $V_{\text{Ga}}$  or  $V_{\text{Ga}}\text{-O}_N$  in its local environment,<sup>12</sup> and the formation of these new  $V_{\text{Ga}}\text{-O}_N$  complexes, for low temperature growth, could be the reason for the fluorescence line narrowing observed in CEES. Moreover, the formation of these complexes could also have an influence on the Eu incorporation, and the lack of precipitation on the surface, by improving the solubility limits of the Eu ions in GaN. Also, since defects are believed to play a role in the energy transfer from GaN to the Eu ions, the appearance of this new defect environment could be responsible for the enhanced PL emission intensity observed under indirect excitation. Therefore, it was believed that this new growth condition would lead to an improved LED.

An LED was grown at 960 °C, and the detailed device structure is given in Fig. 5(a). The current-voltage and output power-current curves of this LED are also given in Fig. 5. The typical current-voltage curve shape for a diode is observed; thus, “good” electrical properties are retained when the growth environment was changed. The maximum output power of this LED was 48  $\mu\text{W}$  with an injection current of 15 mA and an input voltage of  $\sim 5.5$  V. On the contrary, another LED that was grown at 1030 °C with the oxygen-free Eu source, and no additional oxygen, was unsuccessful. This is likely due to the previously observed EuN precipitation. Therefore, a reference LED with the same structure and similar Eu concentration, but grown with  $\text{Eu}(\text{DPM})_3$ , and the known optimal growth conditions for that source,<sup>6</sup> was used for output power comparison. The reference LED’s maximum power was 17  $\mu\text{W}$ ,<sup>6</sup> meaning that the new growth environment resulted in a

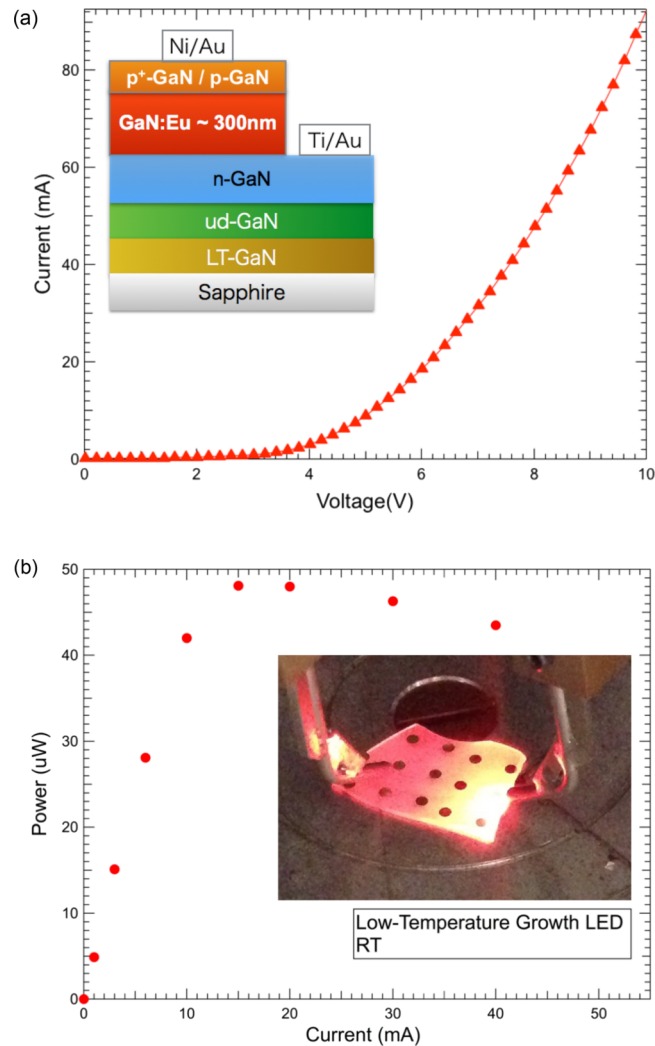


FIG. 5. (a) Device structure and current-voltage curve of a LED grown at 960 °C, with  $\text{EuCp}^{\text{pm}}_2$ . The structure of this LED is as the same as that of the reference LED grown at 1030 °C, with  $\text{Eu}(\text{DPM})_3$ . The current-voltage curve suggests that this LED has good electrical properties, characteristic of a diode. (b) Power-current curve for the low temperature LED. The maximum output power of this LED was 48  $\mu\text{W}$  with an injection current of 15 mA and an input voltage of  $\sim 5.5$  V. This represents nearly a 3-fold improvement in output intensity as compared to the reference LED, grown with the traditional Eu source ( $\text{Eu}(\text{DPM})_3$ ), under the optimal conditions, and having a similar Eu concentration.

nearly 3-fold improvement in output intensity. These results indicate that the increased PL emission intensity has been successfully translated to an increase in EL emission intensity, and that the new OMVPE centers can be excited by current injection as well as indirect excitation. An LED was also fabricated using the 900 °C growth condition. The maximum output power of this LED was 27  $\mu\text{W}$  at 20 mA. This result seems reasonable given the difference in PL intensity between the samples grown at 900 °C and 960 °C, mentioned above.

In conclusion, we have developed a new growth condition for GaN:Eu. By using an oxygen-free Eu source, and reducing the growth temperature, we intentionally introduced a new defect environment for the Eu ions. This new environment was more favorable for stable Eu incorporation, which led to the lack of precipitation observed on the sample surfaces. Using the technique of CEES, it was determined that these new Eu local structures were slight variations of the OMVPE7 center, which also led to a doubling of the PL emission intensity under indirect excitation. The new centers were also easily excited by current injection, which resulted in a  $\sim 3$  times increase in the emission intensity from a GaN:Eu LED, as compared to the reference LED, under similar

operating conditions. Thus, low temperature growth is a promising development for GaN:Eu-based red LEDs.

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