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Investigation of optical gain in Eu-doped GaN thin film grown by OMVPE method

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We prepare and optically characterize a thin film of GaN:Eu. Room temperature intense emission band at around 620 nm is observed, corresponding to \( ^5D_0 \rightarrow {^7}F_2 \) electronic dipole transition of Eu\(^{3+} \) ions in the GaN host material. At lower temperatures, three components, at 621, 622, and 623 nm, arising from different Eu\(^{3+} \) optical centers, can be distinguished. Using a combination of variable stripe length (VSL) and shifting excitation spot (SES) methods we investigate optical gain of this Eu-related PL band at room temperature and determine its lower limit to be approximately 14 cm\(^{-1} \). © 2016 Publishing services by Elsevier B.V. on behalf of Vietnam National University, Hanoi. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

1. Introduction

Rare-earth (RE) doped III–V semiconductors are playing an important role in opto-electronic devices, being considered for, e.g., full-color displays and lighting components [12]. Among them, Eu-doped GaN (GaN:Eu) is interesting for its bright red emission at around 620 nm [3–8]. The advantages of this material come from optical properties of Eu dopants facilitating intense and sharp photoluminescence (PL) spectra due to radiative recombination within the intra-4f shell (4f\(^6\) configuration) of trivalent Eu\(^{3+} \) ions. The crystal-field perturbation by the host matrix lifts partly or completely the degeneracies of the 25s–11g levels [9]. In addition, GaN host material allows a high doping concentration of Eu\(^{3+} \) ions without segregation.

In the past, significant differences in the Eu-related PL properties have been observed depending on sample preparation methods. Fleischman et al. [10] investigated GaN:Eu samples with different growth and doping conditions. The authors identified nine different incorporation sites of Eu\(^{3+} \) ions in GaN. Three types of centers were classified: (1) sites that are dominantly excited through shallow defect traps; (2) sites that are excited through deep defect traps; (3) sites that can be excited only by direct absorption within the 4f-shell, and not at all via the host. The latter category included the majority site, in which the Eu\(^{3+} \) ions are not in the vicinity of trapping centers. The efficiency of the excitation was the highest for the deep traps. Woodward et al. [11] have reported that the bright red emission comes from high excitation efficiency of optically active Eu\(^{3+} \) ion sites with a low relative abundance of less than 3%, while the majority site exhibits low energy transfer efficiency, with high relative abundance more than 97%. In addition, internal and external quantum efficiency of GaN:Er have been investigated [12].

Development of light amplifying devices requires more detailed understanding of the incorporation, excitation, emission as well as optical gain properties of Eu\(^{3+} \) ions. In this study, we present results of our recent research on optical properties of the Eu-doped GaN sample grown by organometallic vapor phase epitaxy (OMVPE) method and estimate the optical gain coefficients for the Eu-related emission.

2. Experimental

The Eu-doped GaN thin-film samples were grown on sapphire (0001) substrates by OMVPE (SR-2000, Taiyo Nippon Sanso). Initial materials for the chemical reaction were trimethylgallium (TMG), ammonia (NH\(_3\)), and tris(dipivaloylmethanato)-europium, C\(_{12}\)H\(_{30}\)O\(_2\)C\(_3\)Eu. The reactor pressure was maintained at 10 kPa during the growth process. Secondary ion mass spectroscopy measurements revealed that the Eu concentration is \( 7 \times 10^{19} \) cm\(^{-3} \), and decreases with the increased growth pressure. The details of the sample preparation can be found elsewhere [4,13].
The emission spectra were investigated with a 266 nm monochromator (M266, Solar Laser System) in combination with a back-thinned type FFT-CCD sensor (SI0140/41-1108, Hamamatsu). PL measurements were carried out at variable temperatures using a continuous-flow cryostat (Optistat CF, Oxford Instruments). For optical excitation, we used a combination of the Nd:YAG laser and tunable optical parametric oscillators, producing pulses of about 10 ns duration at 100 Hz repetition rate (Solar Laser Systems) in a 210–1800 nm range as pumping sources. The time-resolved PL experiments were performed with a thermo-electrically cooled photomultiplier tube (Hamamatsu) in the time-correlated single-photon counting mode. The overall time resolution was 10 ns, being limited by the excitation laser pulse duration. The optical gain experiments were carried out at room temperature by a combination of variable stripe length (VSL) [14] and shifting excitation spot (SES) [15] methods. Details of this experimental approach can be found elsewhere [16].

3. Results and discussion

Fig. 1 shows a PL spectrum of the Eu-doped GaN at room temperature under a pulsed laser illumination with photon energy of 3.5 eV (355 nm) providing band-to-band excitation of GaN host material. We see that the PL spectra exhibit numerous emission peaks in the investigation range, due to \( {^5}D_0 \rightarrow {^7}F_j \) and \( {^5}D_1 \rightarrow {^7}F_j \) (\( j = 0, 1, 2, 3, 4, 5, 6 \)) transitions in Eu\(^{3+}\) ions [9], with their intensities increasing with excitation flux (data not shown).

The intense red emission band at 620 nm comes from \( {^5}D_0 \rightarrow {^7}F_2 \) electronic dipole transition and often sensitive to the chemical bonds in the vicinity of Eu\(^{3+}\) ions. Emission band centered at 590 nm is from \( {^5}D_0 \rightarrow {^7}F_1 \) magnetic dipole transition and hardly varies with changes in crystal field surrounding Eu\(^{3+}\) ions. PL intensity ratio of the electric dipole \( {^5}D_0 \rightarrow {^7}F_2 \) and the magnetic dipole \( {^5}D_0 \rightarrow {^7}F_1 \) transitions indicates the asymmetry or distortion degree of the local environment of Eu\(^{3+}\) ions in the sample. In the investigated sample we find the ratio of 20:1, which is larger than the found for Eu\(^{3+}\) ions in other host materials, e.g., in SnO\(_2\) [17].

Fig. 2 presents the temperature dependence of emission band corresponding to \( {^5}D_0 \rightarrow {^7}F_2 \) electronic dipole transition. Three peaks at around 621, 622, and 623 nm (peak 1, 2, and 3, respectively) can be identified at low temperature and might originate from different optically active Eu\(^{3+}\) ions. Wave functions with the same symmetry could mix under the influence of the crystal field.

![Fig. 1. PL spectra of Eu-doped GaN at room temperature under pulsed laser illumination. The excitation photon energy at 3.5 eV is large enough for band-to-band excitation of GaN. Inset is partial energy diagram of Eu\(^{3+}\) ions.](image1)

![Fig. 2. Dependence of Eu-related PL spectra on temperature. Three identified peaks at around 621, 622, and 623 nm (peak 1, 2, and 3) can be seen at low temperature. Inset is the temperature dependence of the peak 1 and peak 2. Solid lines are B-spline connects for eyes-guiding purpose.](image2)

[9]. Different experimental temperatures facilitate the changes in the lattice constants, consequently exert the influence on the crystal field surrounding the optically active Eu\(^{3+}\) ions. This may lead to the redshift of peak 3. The different optical sites of the Eu\(^{3+}\) dopants are also examined by time-resolved spectroscopy in the next part. Inset of the Fig. 2 is the temperature dependence of the peak 1 and peak 2. Solid lines are B-spline connects for eyes-guiding purpose. Two steps at experimental temperatures at 100 and 240 °C can be clearly seen. These may relate to excitation and de-excitation processes with different ionization energies [18].

Fig. 3 presents different time-resolved spectra of the Eu\(^{3+}\)-related PL intensities at 4.2 K. Inset shows the enlarged spectra in the initial time window of 100 ns. While all the emission peaks have the same life time of \( \tau \approx 230 \) μs, there is a difference in the rise time of PL intensities at less than a few μs time scale. We see that the emission peak at 621 nm appears almost instantly upon pump pulse, whereas for the emission peaks at 622 and 623 nm an initial rise can be distinguished. These different dynamics indicate different origins of excitation from different optically active Eu\(^{3+}\) ions. For the emission peak at 621 nm, excitation might proceed

![Fig. 3. Different time-resolved spectra of the Eu\(^{3+}\)-related PL intensities at 4.2 K. All the emission peaks have the same life time of \( \tau \approx 230 \) μs. Inset shows the enlarged spectra in the initial time window of 100 ns.](image3)
directly to the emitting state of Eu$^{3+}$ ions, while for the emission peaks at 622 and 623 nm, the excitation may proceed via higher excited states of Eu$^{3+}$ ions and/or via related defect states of the host. It takes time ($\mu$s) for the higher excited states/defect states to transfer the energy to the emitting state for the radiative recombination at 622 and 623 nm, accordingly with the initial rise of the PL intensity with time.

Fig. 4 shows VLS and integrated SES intensities at room temperature for Eu-related PL at 620 nm with different length or distance from the edge of sample. PL spectra in the SES and VLS experiments are shown in the inset. In this experimental data, the integrated SES intensity has been normalized for the first three points. From the shapes of the VSL and the integrated SES intensities, we observe an optical gain behavior when the VSL goes above the integrated SES intensity at the distance or length of about 0.5 mm. However, no sign of PL spectral narrowing has been observed. The intensity of the amplified spontaneous emission passing to the end of the excitation length $l$ is given by

$$I_{VLS} = \text{Const} \frac{e^{G l} - 1}{G},$$

where $G$ is the net optical gain. $G$ can be taken from a direct fit or by comparing $I_{VLS}(l)$ and $I_{VLS}(2l)$. In the latter case we have

$$\frac{I_{VLS}(2l)}{I_{VLS}(l)} = \frac{e^{2G l} - 1}{e^{G l} - 1} = e^{G l} + 1.$$  \hspace{1cm} (2)

Taking a logarithm on both sides, we have

$$G = \frac{l}{\ln(\frac{I_{VLS}(2l)}{I_{VLS}(l)} - 1)}.$$  \hspace{1cm} (3)

Applying the Eq. (3) to the experimental data shown in Fig. 4 we can evaluate the optical gain. The calculated optical gains with length $l$ are presented in Table 1, with a maximum net gain being about 14 cm$^{-1}$. We find that the optical gain in this case is not constant and depends on distance. This is typically related to material inhomogeneity which however is not the case of the high-quality GaN:Eu layers investigated here. Consequently we assign this effect to additional effect which might arise, such as wave-guiding, confocal effects or diffraction of the light coupling [16]. Influencing the experimentally determined net gain value.

Table 1: Optical gains against the excitation length of the VSL signals following Eq. (3) with the assumption that $G$ is independent from the excitation length $l$.

<table>
<thead>
<tr>
<th>Length (mm)</th>
<th>0.48</th>
<th>0.72</th>
<th>0.96</th>
<th>1.20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optical gain (cm$^{-1}$)</td>
<td>4.0</td>
<td>14.1</td>
<td>11.6</td>
<td>5.8</td>
</tr>
</tbody>
</table>

4. Conclusion

In conclusion, we have shown that optical gain can be obtained in high-quality GaN:Eu layers. The enhancement is observed for the PL due to radiative recombination within intra-4f electron shell of Eu$^{3+}$ ions. By the combination of VSL and SES methods, we have determined the lower limit for the optical gain of 14 cm$^{-1}$ for 620 nm PL emission at room temperature.

Acknowledgment

This paper is dedicated to the memory of Dr. Peter Brommer — a former physicist of the University of Amsterdam — who passed away on March 23, 2016.

References