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

Ha, N.N.; Nishikawa, A.; Fujiwara, Y.; Gregorkiewicz, T.

Published in:
Journal of Science: Advanced Materials and Devices

DOI:
10.1016/j.jsamd.2016.06.004

Link to publication

Creative Commons License (see https://creativecommons.org/use-remix/cc-licenses):
CC BY

Citation for published version (APA):
Ha, N. N., Nishikawa, A., Fujiwara, Y., & Gregorkiewicz, T. (2016). Investigation of optical gain in Eu-doped GaN thin film grown by OMVPE method. Journal of Science: Advanced Materials and Devices, 1(2), 220-223. https://doi.org/10.1016/j.jsamd.2016.06.004

General rights
It is not permitted to download or to forward/distribute the text or part of it without the consent of the author(s) and/or copyright holder(s), other than for strictly personal, individual use, unless the work is under an open content license (like Creative Commons).

Disclaimer/Complaints regulations
If you believe that digital publication of certain material infringes any of your rights or (privacy) interests, please let the Library know, stating your reasons. In case of a legitimate complaint, the Library will make the material inaccessible and/or remove it from the website. Please Ask the Library: https://uba.uva.nl/en/contact, or a letter to: Library of the University of Amsterdam, Secretariat, Singel 425, 1012 WP Amsterdam, The Netherlands. You will be contacted as soon as possible.

UvA-DARE is a service provided by the library of the University of Amsterdam (http://dare.uva.nl)

Download date: 25 Oct 2020
Investigation of optical gain in Eu-doped GaN thin film grown by OMVPE method

Ngo Ngoc Ha a, c, *, Atsushi Nishikawa b, Yasufumi Fujiwara b, Tom Gregorkiewicz c

* Corresponding author. International Training Institute for Materials Science (ITIMS), Hanoi University of Science and Technology (HUST), No. 1 Dai Co Viet, Hanoi, Viet Nam
E-mail address: hann@itims.edu.vn (N.N. Ha).
Peer review under responsibility of Vietnam National University, Hanoi.

A R T I C L E   I N F O
Article history:
Received 25 May 2016
Received in revised form 6 June 2016
Accepted 6 June 2016
Available online 11 June 2016

ABSTRACT
We prepare and optically characterize a thin film of GaN:Eu. Room temperature intense emission band at around 620 nm is observed, corresponding to $^5D_0 \rightarrow ^7F_2$ 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 optoelectronic 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 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 $^{2S+1}L_J$ 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$_3$H$_7$H$_9$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 (S10140/41-1108, 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 $^5D_0 \rightarrow ^7F_{1-6}$ and $^5D_1 \rightarrow ^7F_{1-6}$ ($J = 0, 1, 2, 3, 4, 5, 6$) 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 $^5D_0 \rightarrow ^7F_2$ electronic dipole transition and often sensitive to the chemical bonds in the vicinity of Eu$^{3+}$ ions. Emission band at around 590 nm is from $^5D_0 \rightarrow ^7F_1$ magnetic dipole transition and hardly varies with changes in crystal field surrounding Eu$^{3+}$ ions. PL intensity ratio of the electric dipole $^5D_0 \rightarrow ^7F_2$ and the magnetic dipole $^5D_0 \rightarrow ^7F_1$ 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 $^5D_0 \rightarrow ^7F_2$ electronic dipole transition. Three peaks at around 621, 622, and 623 nm (peak 1, 2, and 3) can be distinguished. These different dynamics indicate 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.

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 $\tau = 230 \mu$s, there is a difference in the rise time of PL intensities at less than few $\mu$s 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...
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 initial rise of the SES signal indicating a fingerprint for net gain. Inset is the PL spectra of the VLS and SES.

Table 1

| Length (mm) | Optical gain (cm$^{-1}$) |
|------------|-------------------------|
| 0.48       | 4.0                     |
| 0.72       | 14.1                    |
| 0.96       | 11.6                    |
| 1.20       | 5.8                     |

On the purely experimental side, we note that mechanical movements during the experiment can cause a mismatch between the SES spot and the VSL differential shifting step. This creates a situation that SES spot can be larger or smaller than shifting step, leading to overlaps or gaps between the SES spots when shifting along the sample. In this case, integrated SES is higher or lower than the VSL signal, especially, for samples of low gain coefficients. As a result, the optical gain may be under- or overestimated. Consequently, the present result can be seen as evidence for the optical gain in GaN:Eu layers, while the more exact determination of the actual gain value will require more elaborate investigations.

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

[1] C. Zhu, Y. Yang, X. Liang, S. Yuan, G. Chen, Rare earth ions doped full-color luminescence glasses for white LED, J. Lumin. 126 (2) (2007) 707–710.
[2] A.J. Steckl, J. Heikenfeld, D.S. Lee, M. Garter, Multiple color capability from rare earth-doped gallium nitride, Mater. Sci. Eng. B Solid State Mater. Adv. Technol. 81 (1–3) (2001) 97–101.
[3] E.E. Nyeen, U. Hönemich, J. Heikenfeld, D.S. Lee, A.J. Steckl, M.J. Zavada, Spectral and time-resolved photoluminescence studies of Eu-doped GaN, Appl. Phys. Lett. 82 (11) (2003) 1655–1657.
[4] A. Nishikawa, N. Furukawa, T. Kawasaki, Y. Terai, Y. Fujiwara, Improved luminescence properties of Eu-doped GaN light-emitting diodes grown by atmospheric-pressure organometallic vapor phase epitaxy, Appl. Phys. Lett. 97 (5) (2010) 2010–2012.
[5] J.H. Park, A.J. Steckl, Laser action in Eu-doped GaN thin-film cavity at room temperature, Appl. Phys. Lett. 85 (20) (2004) 4588–4590.
[6] J.H. Park, A.J. Steckl, Demonstration of a visible laser on silicon using Eu-doped GaN thin films, J. Appl. Phys. 98 (5) (2005) 50–52.
[7] M. Pan, A.J. Steckl, Red emission from Eu-doped GaN luminescent films grown by metalorganic chemical vapor deposition, Appl. Phys. Lett. 83 (1) (2003) 9–11.
[8] T. Andreev, N.Q. Liem, Y. Hori, M. Tanaka, O. Oda, D.L.S. Dang, B. Daudin, Optical transitions in Eu$^{3+}$ ions in GaN:Eu grown by molecular beam epitaxy, Phys. Rev. B - Condens. Matter Mater. Phys. 73 (19) (2006) 3–8.
[9] K. Binnemans, Interpretation of europium(III) spectra, Coord. Chem. Rev. 295 (2015) 1–45.
[10] Z. Fleischman, C. Munasinghe, A.J. Steckl, A. Wakahara, J. Zavada, V. Dierolf, Excitation pathways and efficiency of Eu ions in GaN by site-selective spectroscopy, Appl. Phys. B Lasers Opt. 97 (3) (2009) 607–618.
[11] N. Woodward, J. Poplawsky, B. Mitchell, A. Nishikawa, Y. Fujiwara, V. Dierolf, Excitation of Eu$^{3+}$ in gallium nitride epitaxial layers: majority versus trap defect center, Appl. Phys. Lett. 98 (1) (2011) 6–8.
[12] W.D.A.M. de Boer, C. McGonigle, T. Gregorkiewicz, Y. Fujiwara, S. Tanabe, P. Stallinga, Optical excitation and external photoluminescence quantum efficiency of Eu(3+) in GaN, Sci. Rep. 4 (2014) 5235.
[13] A. Nishikawa, T. Kawasaki, N. Furukawa, Y. Terai, Y. Fujiwara, Room-temperature red emission from a p-type/europium-doped/n-type gallium nitride light-emitting diode under current injection, Appl. Phys. Express 2 (7) (2009) 2–4.
[14] K.L. Shaklee, R.E. Nahory, R.F. Leheny, Optical gain in semiconductors, J. Lumin. 7 (C) (1973) 284–309.

[15] N.N. Ha, K. Dohnalová, T. Gregorkiewicz, J. Valenta, Optical gain of the 1.54 μ emission in MBE-grown Si:Er nanolayers, Phys. Rev. B 81 (19) (2010) 195206.

[16] N.N. Ha, Towards Optical Amplification for Silicon Photonics, PhD thesis, Univ. Amsterdam, 2012.

[17] B.Q. Thanh, N.N. Ha, T.N. Khiem, N.D. Chien, Correlation between SnO₂ nanocrystals and optical properties of Eu³⁺ ions in SiO₂ matrix: relation of crystallinity, composition, and photoluminescence, J. Lumin. 163 (2015) 28–31.

[18] D.T.X. Thao, C.A.J. Ammerlaan, T. Gregorkiewicz, Photoluminescence of erbium-doped silicon: excitation power and temperature dependence, J. Appl. Phys. 88 (3) (2000) 1443.