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Materials Science and Engineering B 146 (2008) 193–195

MATERIALS SCIENCE & ENGINEERING B

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Spectroscopic studies of Er-centers in MOCVD grown GaN layers highly doped with Er

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Abstract

We report on the high-resolution photoluminescence (PL) and electron spin resonance (ESR) studies of highly Er-doped (2×10^{20} to 2×10^{21} cm^{-3}) MOCVD grown GaN epilayers. The high-resolution Fourier transform of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ PL of Er^{3+} near 1.5 μm, site-selective PL and PL excitation measurements show that in MOCVD grown GaN only one type of Er-centers exists. This conclusion has been confirmed by ESR measurements. In ESR the axial Er^{3+} spectrum was observed with $g_{||} = 2.861$ and $g_{\perp} = 7.645$ characteristic for substitutional Er ions at Ga sites (C_{3V} symmetry). Angular dependence of the ESR did not point to the existence of other centers.
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Keywords: Gallium nitride; Erbium; Photoluminescence; Site-selective spectroscopy

1. Introduction

Erbium-doped GaN has been widely investigated due to the potential applications in optoelectronics [1–3]. Er-doped GaN is one of the most promising systems with a view to room temperature operation [4] in the infrared as well as in the visible, as thermal quenching of the Er emission is reduced in comparison with other semiconductors with smaller band gaps [5]. A majority of the research has been devoted to the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ emission of Er^{3+} ions occurring at 1.54 μm, as this wavelength corresponds to the minimum loss and dispersion in silica fibers for optical communications.

As the emission of Er^{3+} is due to intra-4f-shell transitions the lines are sharp and the wavelength is insensitive to temperature, which makes the system particularly suitable for studies of individual centers of erbium. The near infrared photoluminescence (PL) spectra of Er^{3+} ions in GaN are usually very complex due to the existence of a variety of different Er-centers. It was found that the number of the observed centers depends on growth and annealing conditions as well as on excitation wavelength (i.e. [6,7]). In ion implanted GaN and in molecular beam epitaxy grown Er-doped layers the number of different centers can be high, up to nine for above the band gap and for below the band gap excitation in the blue–green range. It has been shown that for this wavelength range indirect excitation via defects or impurities is the dominant excitation mechanism of Er ions [8,9]. In spite of the existence of numerous centers it seems that most of Er atoms are involved in the formation of one type of center only, as for site-selective resonant pumping to the $^4I_{9/2}$ and $^4I_{11/2}$ states only one type of center was detected [10,11] even if at short wavelength excitation other Er-centers were observed.

In this paper we show using the high-resolution site-selective PL and electron spin resonance (ESR) that in Er-doped MOCVD-grown GaN only a single type of Er-center exists even for the Er concentration as high as 2×10^{21} cm^{-3}.

2. Experimental

Samples used in this studies were MOCVD GaN:Er epilayers grown on sapphire. GaN samples were uniformly doped across the layers with erbium to concentrations ranging from 2×10^{20} cm^{-3} up to 2×10^{21} cm^{-3}. Details of the growth conditions of structures doped in situ were described in paper [12]. A control GaN sample was also grown by MOCVD method on sapphire substrate. Erbium was implanted at an energy of 300 keV to a dose of 10^{13} cm^{-2}. The peak concentration of Er

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doi:10.1016/j.mseb.2007.07.032

in the implanted GaN was $\sim10^{18}$ cm^{-3}. After implantation the sample was annealed at 1000 °C in nitrogen gas flow.

The wide forbidden gap of GaN allowed us to perform site selective and PL excitation (PLE) measurements using a tunable Ti:sapphire laser pumped with an argon laser. The PL was also excited with different UV and visible lines of an Ar laser. The high-resolution PL spectra were detected using a Bomem DA3 Fourier Transform (FTIR) spectrometer equipped with a liquid-nitrogen cooled Ge detector and for PLE measurements a standard monochromator was used. GaN/sapphire structures were studied by means of electron spin resonance (ESR) technique, using a Bruker X-band spectrometer operating at a microwave frequency of ∼9.42 GHz.

3. Experimental results

Fig. 1 shows the comparison of PL of erbium excited at 333 nm (above the band gap), 514 nm (off-resonance), and resonantly at 809.2 nm and measured at liquid helium temperature. As it is seen the spectra are in principle the same in contrast with the results for implanted GaN [2,11]. At resonant pumping the PL lines are narrower than at UV excitation. It indicates that the PL lines are nonuniformly broadened due to the high doping level and at resonant excitation only a subset of centers may absorb the pump light directly.

In Fig. 2 the PLE spectra corresponding to the $^4I_{15/2} \rightarrow {}^4I_{9/2}$ absorption transitions of Er^{3+} measured at 5 K in an in situ doped sample and in a control sample implanted with 10^{13} cm^{-2} of Er and annealed at 1000 °C are compared. The spectra were detected at 1537.3 nm, the strongest line of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ emission observed at 5 K. As it is seen both spectra reveal the same major lines and only minor differences between the two can be noticed. The PLE spectrum of a MOCVD sample is nonuniformly broadened as the concentration of erbium is two orders of magnitude higher than in the implanted sample.

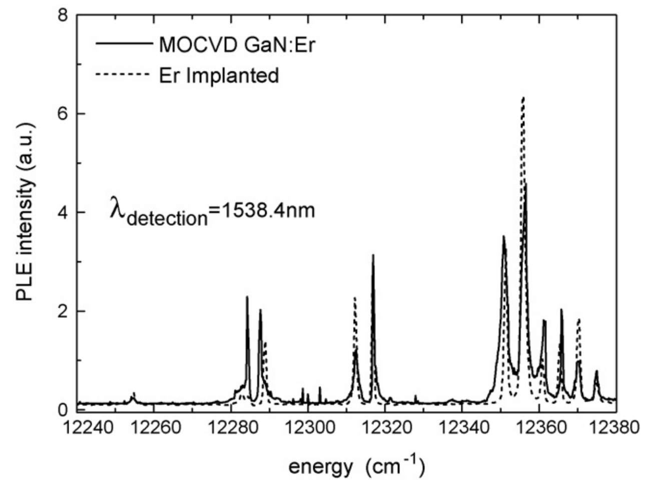

Fig. 2. Comparison of PLE spectra for in situ doped and implanted GaN. Detection wavelength is λ = 1537.3 nm.

The numbers of lines detected in PL (Fig. 1) and PLE (Fig. 2) spectra are higher than the expected maximum numbers for a single low symmetry center (eight in PL, and five in PLE for the $^4I_{9/2}$ state). As it is seen from the energy level diagram in Fig. 3 the energy intervals between two lowest levels in the $^4I_{15/2}$ ground and the $^4I_{13/2}$ emitting state are 4.5 cm^{-1} and 7 cm^{-1}, respectively. Therefore, even at liquid helium temperature the second lowest sublevels are populated and take part in PL, or

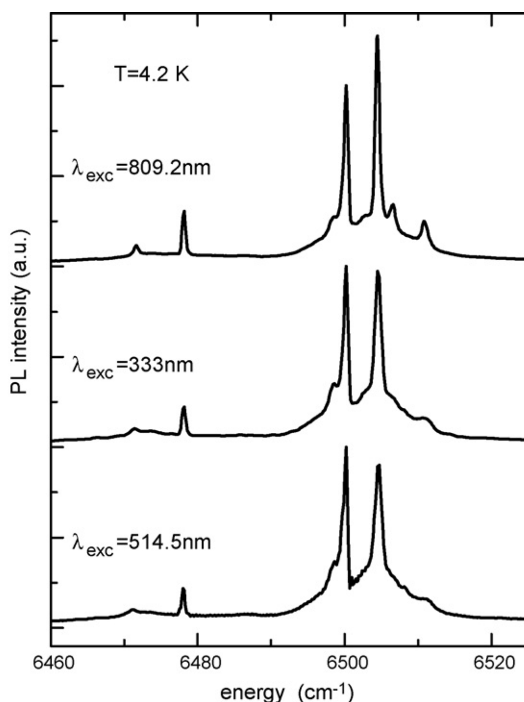

Fig. 1. Comparison of the $^4I_{15/2} \rightarrow {}^4I_{9/2}$ PL of Er^{3+} for UV, 514 nm, and resonant excitation at 809.2 nm for in situ doped GaN.

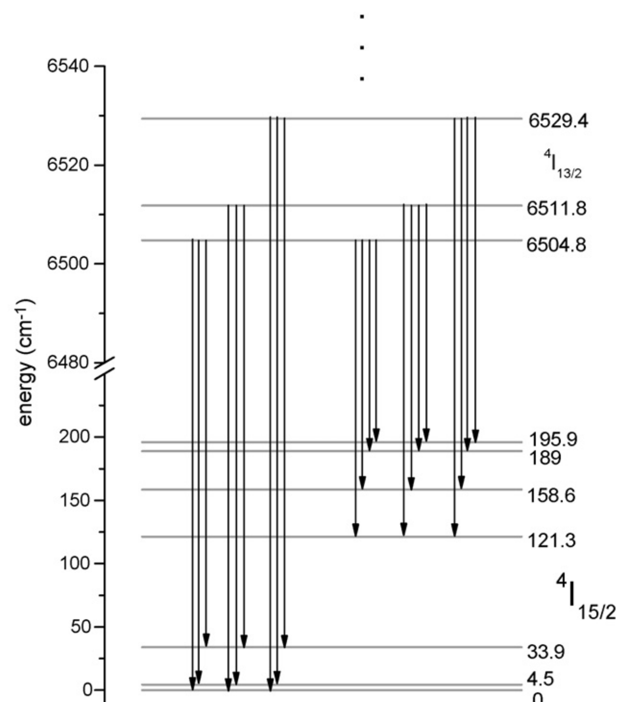

Fig. 3. Energy level diagram for the ground and first excited states of Er^{3+} ions in GaN.

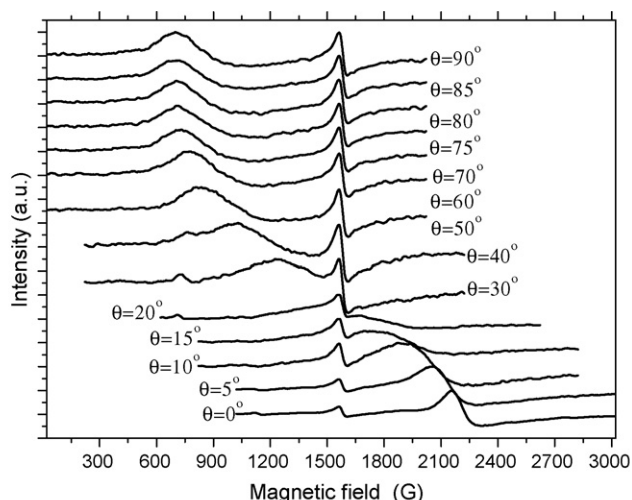

Fig. 4. Angular dependence of ESR signal for Er^{3+} ions in situ doped GaN.

absorption in case of PLE experiments. (Detailed analysis of Stark splitting of Er^{3+} ions was presented in our previous papers [10,11].)

Angular dependence of the ESR spectra obtained for in situ doped GaN with a concentration of Er ions of 2×10^{21} cm^{-3} measured at 5 K are presented in Fig. 4. Such dependence identifies the spectra as originating from Er^{3+}-centers with axial symmetry. The angular evolution of the ESR signal clearly points to the existence of one dominant center only as we could not find any signs for the existence of other centers. The Er spectra are broad and therefore the much weaker (30 times) hyperfine components for $I = 7/2$ cannot be observed.

In Fig. 5 the g^2 value calculated for different angles of the magnetic field and c-axis are shown. From these results the best fit values of $g_\perp$ and $g_{||}$ have been calculated and they are 7.86 and 2.86, respectively, in good agreement with data of Palczewska et al. [13] obtained for bulk GaN-doped with erbium. The average value $g_{av} = 1/3(2g_\perp + g_{||})$ is 6.2 and is close to a value of 6.0 calculated for substitutional Er at Ga sites when Γ_7 is the lowest state [13] in the $^4I_{15/2}$ ground multiplet.

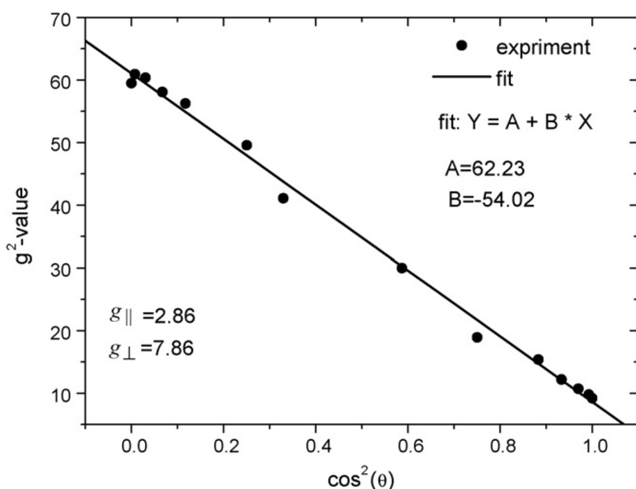

Fig. 5. Linear fit of the g^2 factor to $\cos^2\Theta$, where Θ is angle between magnetic field H and c-axis.

4. Discussion and summary

Luminescence and EPR data presented in this work give clear evidence that in the in situ doped GaN only one dominant type of Er-centers exists even for Er concentration as high as 2×10^{21} cm^{-3}. No other centers were observed at UV, blue–green and resonant excitation in a striking difference with implanted GaN where many centers were found even for Er concentrations orders of magnitude lower. As the Stark energy levels determined from the PL and PLE spectra for implanted and in situ doped GaN coincide, we conclude that in both materials the dominant centers have the same structure. Point charge model calculations performed in work [10] suggest that the symmetry of the center is C_{3V}, in agreement with the substitutional location of Er atoms at Ga sites [14] in hexagonal GaN.

The existence of only one center with axial symmetry has been confirmed by ESR measurements. Analysis of the g factor revealed that the ESR signal comes from substitutional erbium at Ga sites and Γ_7 is the lowest state in the $^4I_{15/2}$ multiplet.

Taking into account the results obtained in this work we conclude that the dominant Er-center in MOCVD grown in situ doped GaN is due to Er at substitutional Ga site. Large width of lines observed in optical and ESR spectra suggests that the presence of nearby Er atoms perturbs the symmetry of substitutional atoms contributing to nonuniform broadening. In spite of the high Er concentration we have not found emission that could be assigned to Er–Er pairs.

Acknowledgement

KSU research is supported by a grant from US ARO.

References

[1] R.G. Wilson, R.N. Schwartz, C.R. Abernathy, S.J. Pearton, N. Newman, M. Rubin, T. Fu, J.M. Zavada, Appl. Phys. Lett. 65 (1994) 22.
[2] S. Kim, S.J. Rhee, X. Li, J.J. Coleman, S.G. Bishop, Appl. Phys. Lett. 71 (1997) 2662.
[3] S. Kim, S.J. Rhee, X. Li, J.J. Coleman, S. Bishop, Appl. Phys. Lett. 76 (2000) 2403.
[4] Y.Q. Wang, A.J. Steckl, Appl. Phys. Lett. 82 (2003) 502.
[5] P.N. Favennec, H. L'Haridon, M. Salvi, D. Moutonnet, Y. Le Guillou, Electr. Lett. 25 (1989) 718.
[6] S. Kim, S.J. Rhee, D.A. Turnbull, E.E. Reuter, X. Li, D.J. Coleman, S. Bishop, Appl. Phys. Lett. 71 (1997) 231.
[7] V. Dierolf, C. Sandmann, J.M. Zavada, P. Chow, B. Herzog, J. Appl. Phys. 95 (2004) 5464.
[8] X. Wu, U. Hommerich, J.D. Mackenzie, C.R. Abernathy, S.J. Pearton, R.N. Schwartz, R.G. Wison, J.M. Zavada, Appl. Phys. Lett. 70 (1997) 2126.
[9] C. Ugolini, N. Nepal, J.Y. Lin, H.X. Jiang, J.M. Zavada, Appl. Phys. Lett. 89 (2006) 051110.
[10] V. Glukhanyuk, H. Przybylińska, A. Kozanecki, W. Jantsch, Opt. Mater. 28 (2006) 746.
[11] H. Przybylińska, A. Kozanecki, V. Glukhanyuk, W. Jantsch, D.J. As, K. Lischka, Physica B 308–310 (2001) 34.
[12] C. Ugolini, N. Nepal, J.Y. Lin, H.X. Jiang, J.M. Zavada, Appl. Phys. Lett. 89 (2006) 151903.
[13] M. Palczewska, A. Wolos, M. Kaminska, I. Grzegory, M. Bockowski, S. Krukowski, T. Suski, S. Porowski, Solid State Commun. 114 (2000) 39.
[14] E. Alves, M.F. da Silva, J.C. Soares, R. Vianden, J. Bartels, A. Kozanecki, Nucl. Instrum. Methods B 147 (1999) 383.