

Synthesis and optical characterization of erbium-doped III-N double heterostructures

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Abstract

We report on the first successful synthesis of Er-doped III-N double heterostructures (DHs) grown on sapphire substrates. AlGaIn layers, with an Al concentration of $\sim 12\%$, were prepared by metalorganic chemical vapor deposition and Er-doped GaN layers by molecular beam epitaxy. The Er concentration was estimated to be $\sim 10^{18} \text{ cm}^{-3}$. GaN:Er/AlGaIn single heterostructures (SHs) and AlGaIn/GaN:Er/AlGaIn DHs were studied using photoluminescence (PL) spectroscopy. Emission lines characteristic of the GaN:Er system (green: 537 and 558 nm, infrared: 1530 nm) were observed in all samples. With UV excitation, the infrared PL from the DHs showed a marked improvement compared to the SHs. The PL intensity increased and the spectra showed less defect-related emission. The enhanced PL properties may be due to more effective confinement of electron-hole pairs in the quantum well region.

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1. Introduction

Wilson et al. [1] were the first to observe optical emission from Er ions incorporated in III-V nitride semiconductors. GaN films were implanted with $\text{Er}^+ + \text{O}^+$ ions and then annealed at $\sim 650\text{--}700^\circ\text{C}$. The Er densities were determined using secondary ion mass spectrometry (SIMS) analysis and the maximum Er density was on the order of 10^{19} cm^{-3} at a depth of $\sim 0.1 \mu\text{m}$. Strong infrared luminescence, centered at $1.54 \mu\text{m}$, was measured from the Er-implanted GaN samples using laser excitation at a wavelength of 457.9 nm . The spectra were centered at $1.54 \mu\text{m}$ and displayed many distinct lines indicative of the allowed transitions between the $^4I_{13/2}$ and the $^4I_{15/2}$ manifolds of the Er^{3+} 4f system. At room temperature, the integrated Er^{3+} luminescence intensity was more than 50% that at 77 K. However, ion implan-

tation introduces considerable damage to the crystal host and post-implantation annealing was required to achieve any Er^{3+} luminescence.

Subsequently, MacKenzie et al. [2] succeeded in growing GaN films doped with Er atoms using a metalorganic molecular beam epitaxy (MOMBE) system with a solid elemental Er source and triethylgallium (TEGa) for the Ga flux. SIMS analysis of the Er-doped GaN layers indicated that Er densities in the $10^{19}\text{--}10^{20} \text{ cm}^{-3}$ range were achieved over a thickness from 0.5 to $1.0 \mu\text{m}$. Later, Steckl and Birkhahn [3] and Birkhahn and Steckl [4] achieved in situ doping of GaN films using solid source MBE (SSMBE). The Er concentration in the GaN film reached $3 \times 10^{20} \text{ cm}^{-3}$. These studies were expanded to yield GaN films doped with other rare earth elements such as Pr, Eu, and Tm [5].

Hömmerich et al. [6] compared the infrared luminescence properties of Er-doped GaN films grown by MOMBE and by SSMBE. Both types of samples displayed characteristic $1.54 \mu\text{m}$ PL resulting from the intra-4f Er^{3+} transitions. With below-gap excitation the samples exhibited very

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similar 1.54 μm PL features and intensities. However, with above-gap excitation, very different PL features and intensities were found. The SSMBE samples exhibited a PL nearly 80 times more intense than that observed from the MOMBE sample. The infrared PL signal was exhibited very stable at temperatures as high as 550 K.

Since GaN has a bandgap of ~ 3.51 eV, it should be possible to observe visible emission from higher excited 4f levels of the Er ions. Steckl and Birkhahn [3] were the first to measure such emission in GaN:Er films prepared by SSMBE [3]. With above-bandgap excitation, these films exhibited intense green PL for transitions from the $^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$ excited levels to the $^4\text{I}_{15/2}$ ground state. The visible luminescence spectra exhibited two primary lines located at 537 nm (2.309 eV) and 558 nm (2.222 eV). None of the GaN:Er films prepared by MOMBE exhibited green emission.

Following these early studies, there have been many efforts to improve the visible and infrared luminescence from GaN films doped with Er and other rare earth ions [7–9]. The demonstration of visible thin-film electroluminescence (TFEL) devices based on this class of materials has stirred wide spread interest for possible applications in full color displays [10]. Prime candidates for red-green-blue (RGB) emission are the rare earth ions Eu^{3+} (red), Er^{3+} (green), and Tm^{3+} (blue). A full-color TFEL phosphor system has been shown to yield high brightness (500–1000 cd/m^2) under direct current operation [11]. These studies have also shown that growth conditions significantly impact the Er^{3+} lattice location and the concentration of optically active Er^{3+} ions.

Here, we report on the first successful synthesis of GaN:Er/AlGaN heterostructures grown through a combination of metalorganic chemical vapor deposition (MOCVD) and molecular beam epitaxy on *c*-plane sapphire substrates. Characteristic visible and infrared emission lines of the GaN:Er system were observed in these samples, even for those with the thinnest Er-doped regions. With UV excitation the infrared PL signal from the double heterostructures (DHs) showed a marked improvement compared to the uncapped, single heterostructures (SHs).

2. Experimental details

The synthesis of the III-N heterostructures was achieved through a multi-stage growth process. First, AlGaN epilayers were grown by MOCVD on sapphire (0001) substrates, as described elsewhere [11]. The n-type layers were ~ 1 μm thick, with an Al content $\sim 12\%$ and a Si doping $\sim 10^{18}$ cm^{-3} . This corresponds to a bandgap of ~ 3.75 eV for the $\text{Al}_{0.12}\text{Ga}_{0.88}\text{N}$ alloy. Subsequently, GaN:Er epilayers were grown by MBE and had an Er concentration of $\sim 10^{18}$ cm^{-3} [12]. Two GaN:Er layer thicknesses were produced, 7 and 200 nm. After this stage, each sample was cut into two parts. One set was reserved for characterization, the other for a second growth of AlGaN by MOCVD. The top AlGaN layer was ~ 200 nm thick, again with $\sim 12\%$ Al.

PL spectra were measured using either the UV argon laser lines (336–363 nm) or a visible argon laser line at 496.5 nm. Infrared PL spectra were recorded using a 1-m monochromator equipped with a liquid-nitrogen cooled Ge detector. The visible PL measurements were made using a thermo-electric cooled photomultiplier tube for detection. The signal was processed using lock-in techniques or a boxcar averager. The obtained PL spectra were not corrected for the spectral response of the set-up.

3. Results and discussion

In Fig. 1 are shown the infrared PL spectra, measured at room temperature, for the 200 nm SH and the corresponding DH. The laser pump wavelength (λ_p) of 496.5 nm overlaps an intra-4f Er^{3+} absorption line ($^4\text{I}_{15/2} \rightarrow ^4\text{F}_{9/2}$) [13]. The energy of the pump photons (2.48 eV) is below the bandgap of both the GaN and the $\text{Al}_{0.12}\text{Ga}_{0.88}\text{N}$ epilayers. As can be seen in Fig. 1, there is little difference in the two spectra. The main emission lines represent those from the Er^{3+} 4f system near 1.54 μm and 1.0 μm . The data indicate that there are optically active Er^{3+} ions in the GaN:Er epilayers and, that the absorption of the pump radiation in the top $\text{Al}_{0.12}\text{Ga}_{0.88}\text{N}$ layers in the DH was minimal. Furthermore, the MOCVD growth of the top layer did not significantly alter the optically activity of the Er^{3+} ions.

The data for the 7 nm SH and the corresponding DH were not as conclusive. The PL signals were weak and no distinct Er^{3+} emission lines could be observed. This may be due to the low excitation cross-section for the Er^{3+} ions under resonant pumping and the very thin Er-doped regions found in these samples.

The PL measurements using the UV lines at ~ 336 – 363 nm yielded different results. The energy of the pump photons

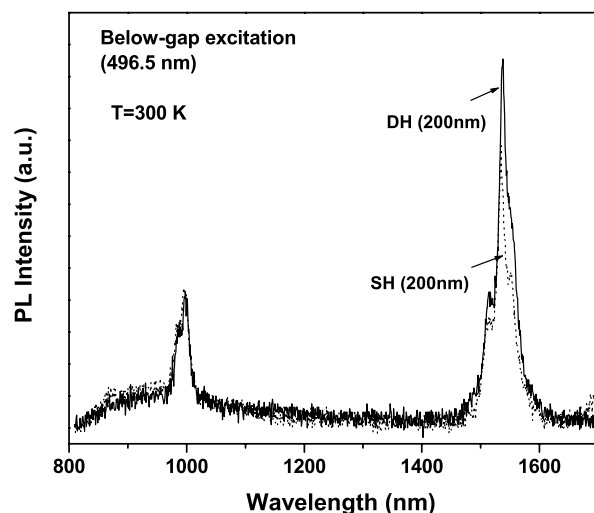


Fig. 1. Infrared PL spectra of a 200 nm GaN:Er/AlGaN SH (dotted line) and a 200 nm AlGaN/GaN:Er/AlGaN DH (solid line). The spectra were measured at 300 K using pump radiation at 496.5 nm.

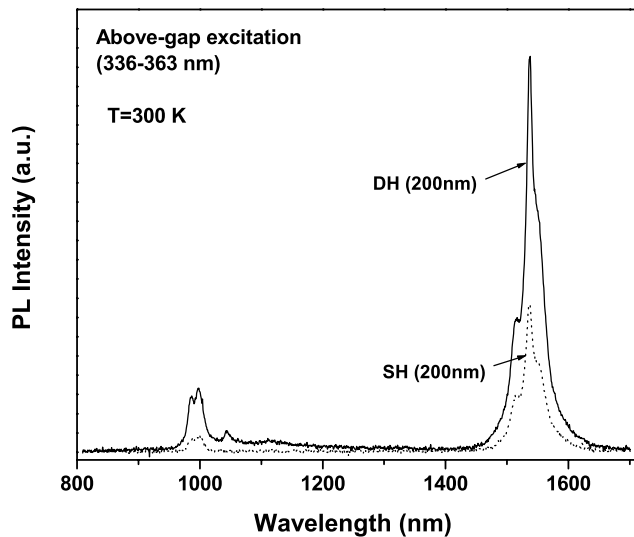


Fig. 2. Infrared PL spectra of a 200 nm GaN:Er/AlGaN SH (dotted line) and a 200 nm AlGaN/GaN:Er/AlGaN DH (solid line). The spectra were measured at 300 K using pump radiation at 336–363 nm.

(3.67–3.40 eV) is above the bandgap of the GaN epilayer, but below that of the $\text{Al}_{0.12}\text{Ga}_{0.88}\text{N}$ epilayer. In this case, the Er^{3+} ions are excited via electron–hole (e–h) pairs that are generated in the GaN:Er epilayer. In Fig. 2 are shown the infrared PL spectra for the 200 nm SH and the corresponding DH. While both spectra have features characteristic of the Er^{3+} system, the intensity from the DH is ~ 3 times that from the SH. Since there may be some absorption of the pump radiation in the $\text{Al}_{0.12}\text{Ga}_{0.88}\text{N}$ cover layer, the actual increase of PL intensity in the DH may be even greater. The improved excitation efficiency of Er^{3+} in the DH seems to be due to better e–h confinement in the GaN:Er epilayer as a result of the band offsets with the $\text{Al}_{0.12}\text{Ga}_{0.88}\text{N}$ epilayers. Rather than recombining at the air–semiconductor interface as in the SH, the e–h pairs in the DH may have a greater probability of recombining near Er-related complexes. In addition, the top $\text{Al}_{0.12}\text{Ga}_{0.88}\text{N}$ epilayer reduces or eliminates surface recombination of the e–h pairs [14].

The data for the 7 nm SH and the corresponding DH also show an improvement with UV pumping. As shown in Fig. 3, the PL spectrum for the 7 nm SH is broad and not characteristic of Er^{3+} emission. The PL spectrum for the 7 nm DH has definite features of Er^{3+} emission near $1.54 \mu\text{m}$. As in the case of the 200 nm DH, confinement of e–h pairs increases the transfer of energy to the Er^{3+} ions. The layer dimensions of the 7 nm DH are such that it is appropriate to use the term quantum well (QW) to describe this structure. With a well thickness of 7 nm and an Al content of 12%, quantum size effects are expected. This would likely lead to the Er ions experiencing a host region with a slightly higher bandgap and to an increase in the e–h lifetime. However, the main improvement in the PL signal appears to be due to a greater confinement of e–h pairs in the GaN:Er region.

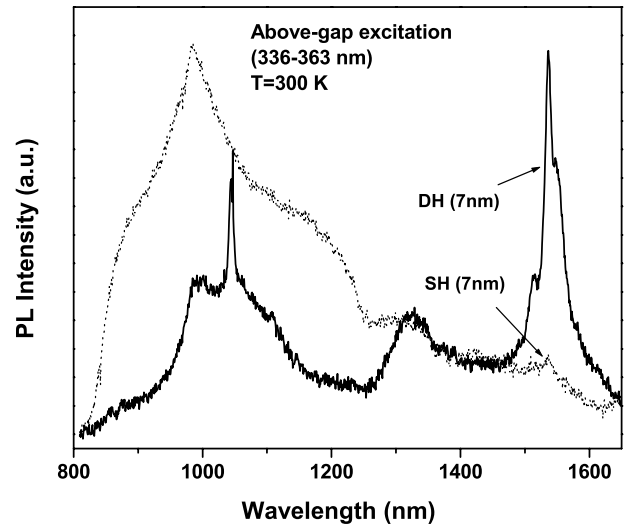


Fig. 3. Infrared PL spectra of a 7 nm GaN:Er/AlGaN SH (dotted line) and a 7 nm AlGaN/GaN:Er/AlGaN DH (solid line). The spectra were measured at 300 K using pump radiation at 336–363 nm.

The PL spectra for the two DHs are compared in Fig. 4. The spectra are quite similar except that the intensity from the 200 nm DH is ~ 4 times greater than that from the 7 nm DH. It is surprising that the thicker DH did not yield a higher intensity compared to the thinner one. For the UV wavelengths of 336–363 nm, the absorption coefficient for undoped GaN is $\sim 10^5 \text{ cm}^{-1}$ [15]. Assuming that the absorption for Er-doped GaN is at least as high, the intensity of the pump radiation is reduced by $\sim 86\%$ before reaching the second interface of the 200 nm DH and by only $\sim 7\%$ before reaching the second interface of the 7 nm DH. Consequently, since the generation of e–h pairs is dependent upon amount of absorbed radiation, the intensity from the 200 nm DH

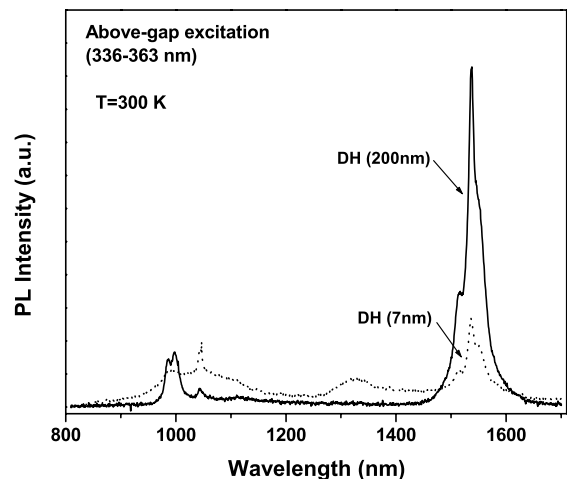


Fig. 4. Infrared PL spectra of two AlGaN/GaN:Er/AlGaN DHs measured at 300 K. The samples were excited with pump radiation at 336–363 nm. The GaN:Er layer was 7 nm in one (dotted line) and 200 nm thick in the other (solid line).

should be ~10–15 times greater than that from the 7 nm DH. The experimental result may be due to greater absorption of the pump radiation in the GaN:Er layer and to the closer proximity of the second heterojunction in the thinner sample.

4. Conclusions

There have been a few previous efforts to introduce rare earth ions in DH or QW regions. Sotta et al. reported on Er + O implantation into Si/SiO₂ quantum wells having a well thickness of 200 nm [16]. They found that the 1.54 μm emission at 10 K was 3–4 times more intense than that from similarly implanted bulk Si samples. Confinement of e–h pairs was cited as the physical mechanism leading to enhanced luminescence. Fujiwara et al. have studied luminescence from GaInP/GaAs:Er, O/GaInP DHs grown by MOCVD. They found the PL intensity at 4.2 K from the DHs was ~3 times higher than that from a SH [14]. They also processed the structures into light emitting diodes (LEDs) measured strong room temperature Er³⁺ luminescence under forward bias [17].

With wide bandgap semiconductors, Lozykowski et al. reported on the implantation of Eu into an AlGaIn/GaN superlattice (SL) [18]. Well thickness in the SL was 4 nm and barrier thickness was 6 nm. Post-implantation annealing was needed to achieve emission from the Eu³⁺ centers. Room temperature luminescence at 622 nm was 58% more intense than that from similarly implanted GaN thin film samples. However, due to the implantation, the Eu ions were located in the AlGaIn barriers as well as in the GaN wells. It is difficult to conclude from their experiments that e–h confinement was responsible for the enhancement. In the present set of experiments, it is more certain that the Er³⁺ ions are located in a single GaN epilayer and that the enhanced luminescence at RT is due to better e–h confinement and reduced surface recombination. The use of MOCVD and MBE growth techniques has permitted the synthesis of precise multilayer SHs and DHs. Such structures are the basic building blocks that can be used to form true Er-doped, AlGaIn/GaN p–n LEDs in the future.

Acknowledgements

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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 (8) (1994) 992–994.
- [2] J.D. MacKenzie, C.R. Abernathy, S.J. Pearton, U. Hömmerich, J.T. Seo, R.G. Wilson, J.M. Zavada, *Appl. Phys. Lett.* 72 (1998) 2710.
- [3] A. Steckl, R. Birkhahn, *Appl. Phys. Lett.* 73 (1998) 1702.
- [4] R. Birkhahn, A.J. Steckl, *Appl. Phys. Lett.* 73 (1998) 2143.
- [5] A.J. Steckl, J.M. Zavada, *MRS Bull.* 24 (9) (1999) 33.
- [6] U. Hömmerich, J.T. Seo, J.D. MacKenzie, C.R. Abernathy, R. Birkhahn, A.J. Steckl, J.M. Zavada, *MRS Fall 1999 Meeting*, Paper W11.65.
- [7] G.S. Pomeroy, P.B. Klein, D.W. Langer (Eds.), *Proceedings of the Materials Research Society on Rare Earth Doped Semiconductors I*, vol. 301, 1993.
- [8] S. Coffa, A. Polman, R.N. Schwartz (Eds.), *Proceedings of the Materials Research Society on Rare Earth Doped Semiconductors II*, vol. 422, 1996.
- [9] J. Zavada, T. Gregorkiewicz, A.J. Steckl (Eds.), *Proceedings of E-MRS Symposium on Rare Earth Doped Semiconductors III*, Spring 2000, *Mater. Sci. Eng. B* 81 (2001).
- [10] A.J. Steckl, J. Heikenfeld, D.S. Lee, M.J. Garter, C.C. Baker, Y. Wong, R. Jones, *IEEE J. Sel. Top. Quant.* 8 (2002) 749.
- [11] J. Li, K.B. Nam, M.C. Nakarmi, J.Y. Lin, H.X. Jiang, *Appl. Phys. Lett.* 81 (2002) 3365.
- [12] SVT Associates, Inc., unpublished.
- [13] G.H. Dieke, *Spectra and Energy Levels of Rare Earth Ions in Crystals*, Wiley, New York, 1968.
- [14] A. Koizumi, N. Watanabe, K. Inoue, Y. Fujiwara, Y. Takeda, *Physica B* 308–310 (2001) 891.
- [15] C.H. Yan, W.H. Yao, J.M. Van Hove, A.M. Wochak, P.P. Chow, J.M. Zavada, *J. Appl. Phys.* 88 (2000) 3463.
- [16] D. Sotta, V. Calvo, H. Ulmer-Tuffigo, N. Magnea, E. Hadji, F. Fournel, J.L. Rouviere, D. Jalabert, H. Moriceau, B. Aspar, *Mater. Sci. Eng. B* 81 (2001) 43.
- [17] Y. Fujiwara, A. Koizumi, Y. Takeda, *European Materials Society Spring Meeting 2003*, Strasbourg, France, Paper J-III.5.
- [18] H.J. Lozykowski, W.M. Jadwisienczak, J. Han, I.G. Brown, *Appl. Phys. Lett.* 77 (2000) 767.