ELSEVIER

Materials Science and Engineering B81 (2001) 127–131

MATERIALS SCIENCE & ENGINEERING B

www.elsevier.com/locate/mseb

Annealing behavior of luminescence from erbium-implanted GaN films

J.M. Zavada [a,*], C.J. Ellis [b], J.Y. Lin [b], H.X. Jiang [b], J.T. Seo [c], U. Hömmerich [c], M. Thaik [c], R.G. Wilson [d], P.A. Grudowski [e], R.D. Dupuis [e]

[a] *US ARL-European Research Office, London NW 1 5TH, UK*
[b] *Kansas State University, Manhattan, KS 66506, USA*
[c] *Hampton University, Hampton, VA 23668, USA*
[d] *Consultant, Stevenson Ranch, CA 91381, USA*
[e] *The University of Texas at Austin, Austin, TX 78712, USA*

Abstract

We have conducted a systematic study of the bandedge and infrared luminescence properties of Er-implanted GaN thin films. The GaN films, grown by metalorganic chemical vapor deposition, were co-implanted with Er and O ions. After implantation, the implanted samples were furnace annealed at temperatures up to 1100°C. Following annealing, the samples were examined for both bandedge luminescence and for infrared luminescence near 1540 nm. It was observed that the bandedge photoluminescence (PL) was significantly reduced in the as-implanted samples. In addition, there was no detectable PL signal near 1540 nm, with either above-bandgap or below-bandgap excitation. Only after annealing at temperatures above 900°C did both the bandedge luminescence and the 1540 nm luminescence become well defined. An optical transition at 3.28 eV was also observed, apparently induced through Er + O implantation. While annealing at higher temperatures resulted in a decrease in the 1540 nm luminescence, emission intensities from the bandedge and the defect level both increased. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Erbium; GaN; Ion implantation; Photoluminescence

1. Introduction

Ion implantation has been widely applied in the doping of semiconductor materials used in integrated electronic circuits and optoelectronic devices. Since implantation is a non-equilibrium process, doping is limited neither by solubility nor by surface chemistry constraints. A high concentration of dopant atoms can be formed in localized regions of the semiconductor host. Consequently, several research groups have used ion implantation to dope III–V nitride semiconductors with rare earth (RE) atoms [1–4]. However, ion implantation of rare earth atoms leads to considerable damage to the GaN crystal and post-implantation annealing is required to observe RE^{3+} luminescence.

Wilson et al. reported the first observations of 1540 nm emission from Er ions implanted into III–V nitride semiconductor films [1]. The GaN films, which were grown on GaAs and on sapphire substrates, were co-implanted with Er and O ions and then annealed at ~650–700°C for 20 min. Several studies have indicated that co-doping the semiconductor with impurity elements, such as O or F, enhances the infrared emission [5–7]. Secondary ion mass spectrometry (SIMS) analysis was used to obtain atomic depth profiles of Er and O in the GaN layers [8]. The SIMS measurements, which were quantified using Er-implanted standards, confirmed that a maximum Er density on the order of 10^{19} cm^{-3} was achieved at a depth of ~0.08 μm.

After ion implantation and annealing, the Er atoms can occupy a number of different sites within the GaN crystal lattice. The exact locations of the implanted Er atoms and the atomic complexes that are formed with annealing have not been fully identified. Alves et al. have examined Er-implanted GaN films using Rutherford backscattering (RBS) analysis [9]. A He ion beam was used to probe the crystallinity of the material and

* Corresponding author. Tel.: +44-20-75144907; fax: +44-20-77241433.
E-mail address: jzavada@usardsguk.army.mil (J.M. Zavada).

0921-5107/01/$ - see front matter © 2001 Elsevier Science B.V. All rights reserved.
PII: S0921-5107(00)00689-9

to detect atoms in interstitial sites. One GaN film was implanted only with Er ions to a fluence of 5×10^{14} cm^{-2}. Another GaN film was implanted with both Er and O ions, each to a fluence of 5×10^{14} cm^{-2}. After furnace annealing for 30 min at 600°C, the RBS data showed that the lattice damage was considerably reduced with a minimum yield along the c-axis of about 12% in the case of the Er + O implanted sample and about 20% for the sample implanted with only Er. In both cases, the Er dip overlapped the host dip, indicating nearly complete occupation of the Er atoms on the Ga sub-lattice.

Torvik et al. performed a detailed photoluminescence (PL) study of GaN films co-implanted with Er and O ions [2]. The films were grown by chemical vapor deposition on R-plane sapphire substrates. Different combinations of fluences for the implants and annealing temperatures were examined. After each annealing stage, the samples were examined for Er^{3+} luminescence using laser excitation at a wavelength of 980 nm. This corresponds to a resonant excitation of the Er^{3+} ions by optical pumping to the $^4I_{15/2}$ manifold. In their experiments, the samples implanted with the highest Er fluence ($\sim 10^{15}$ cm^{-2}) yielded the strongest PL intensity. In a subsequent work, Torvik et al. measured the luminescence of Er-doped GaN films using a laser at a wavelength of 360 nm [10]. This represents an indirect excitation of the Er^{3+} ions by electron-hole pairs created with above-bandgap radiation. However, the resulting emission near 1540 nm was not as intense as that under resonant excitation.

In spite of these studies, it is not clear what are the optimum implantation and annealing conditions. Furthermore, questions remain as to why the Er^{3+} luminescence disappears after annealing at higher temperature, when in fact, the SIMS depth profile for the Er distribution is unaltered and the quality of the GaN host seems to improve. In this study, we have investigated the bandedge and infrared luminescence properties of GaN thin films co-implanted with Er and O ions. The experimental data indicate a complicated interplay between implantation parameters and annealing procedures.

2. Experimental details

The GaN films used in these experiments were grown by metalorganic chemical vapor deposition (MOCVD) on c-plane sapphire substrates. Details of the MOCVD growth have been described earlier [11]. The epilayers were ~ 0.8 μm thick and were co-implanted with Er and O ions. Er implantation was done at an energy of 300 keV to a dose of 5.7×10^{13} cm^{-2}. O implantation was done at an energy of 40 keV to a dose of 1.2×10^{15} cm^{-2}. SIMS analysis of the implanted GaN film was used to quantify the actual concentrations after implantation. After implantation, the samples were cut into small pieces that were then annealed for 10 min in a nitrogen ambient at various temperatures ranging from 800 to 1100°C. PL measurements were performed on each of the GaN pieces.

The excitation source for the bandedge PL measurements consisted of laser pulses at a wavelength of 290 nm with 10 ps width and 9.5 MHz repetition rate. The PL emission was collected and analyzed with a 1.3 m grating monochromator equipped with a micro-channel plate photomultiplier tube used in a single photon counting mode.

PL spectra near 1540 nm were measured using the UV argon laser lines (336–363 nm) for above-bandgap excitation and with a visible HeCd laser line (442 nm) for below-bandgap excitation. Infrared PL spectra were recorded using a 1-m monochromator equipped with a liquid-nitrogen cooled Ge detector. The signal was processed using lock-in techniques. The obtained PL spectra were not corrected for the spectral response of the setup.

The SIMS measurements for the Er atoms were made using O_2^+ ion bombardment and positive secondary ion detection. SIMS measurements for impurity elements such as O and C atoms were made using Cs^+ ion bombardment and negative secondary ion detection.

3. Photoluminescence spectroscopy

Photoluminescence spectroscopy has been the main optical technique used to characterize the emission of RE ions in semiconductor materials. This technique involves optical excitation of the RE ions and measurement of the emission as a function of intensity and energy. In a wide bandgap semiconductor host, there are at least three different methods for optical excitation of the RE ions. The first consists in using an optical source having above-bandgap energy. This method leads to generation of electron-hole pairs, some of which may transfer energy to RE ions leading to excitation of the 4f electrons. This process is an indirect excitation of the RE^{3+} ions. In the second method, RE ions can be excited directly by the optical source radiation, provided that the energy of the radiation is resonant with one of the higher energy states of the RE ion. A third method involves an indirect excitation of the RE ions through a carrier-mediated process involving defects in the host crystal [3,12,13]. Defects and impurity elements in the GaN host lead to broad, below-bandgap absorption bands that can provide an effective excitation mechanism of the Er^{3+} ions.

3.1. Infrared luminescence

In Fig. 1 are shown room temperature (RT) Er^{3+} PL spectra over the range of 1400–1700 nm for the Er-implanted GaN samples annealed up to 1100°C. The spectra are displaced to permit easier viewing. The Er^{3+} ions were excited using a HeCd laser at a wavelength of 442 nm, corresponding to below-bandgap excitation. As shown in Fig. 1, no PL signal was detected in the as-implanted sample. After annealing at 800°C, there was a detectable PL signal near 1540 nm, indicative of the transition between the $^4I_{13/2}$ and the $^4I_{15/2}$ manifolds of the Er^{3+} system. The PL signal became more intense with annealing at higher temperatures and reached a maximum after annealing at 900°C. Annealing above 900°C resulted in a diminished Er^{3+} PL signal that became undetectable after annealing at 1100°C.

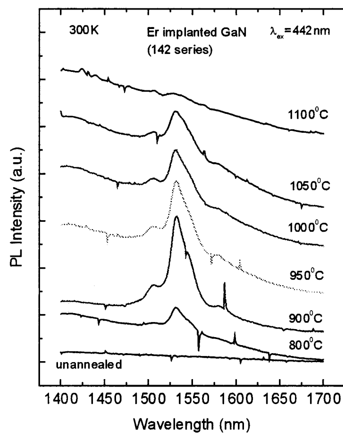

Fig. 1. Infrared PL spectra, measured at room temperature, of Er-implanted GaN as a function of annealing temperature. The Er^{3+} ions were excited using a laser source (442 nm) corresponding to below-bandgap excitation.

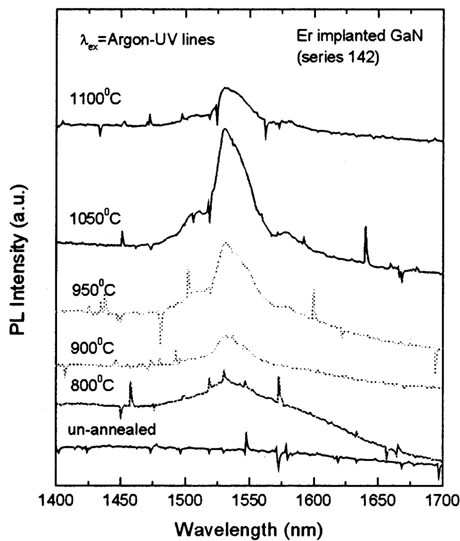

Fig. 2. Infrared PL spectra, measured at room temperature, of Er implanted GaN as a function of annealing temperature. The Er^{3+} ions were excited using a laser source (336–363 nm) corresponding to above-bandgap excitation. The spectra are displaced to permit easier viewing.

In general, a number of different sites are available to the Er atoms after ion implantation. The locations of the implanted Er atoms in the GaN host matrix can change with annealing, as well as the local configuration of the Er^{3+} ions. Prior studies have shown that different Er^{3+} complexes have different absorption characteristics and lead to different PL spectra near 1540 nm [13]. The implantation-induced damage in the GaN host may also produce absorption of the luminescence near 1540 nm. Annealing at temperatures above 800°C may be necessary to reduce the damage-related absorption to low enough levels to permit detection of the PL near 1540 nm. It seems that the Er^{3+} complexes that lead to the spectra shown in Fig. 1 change with annealing above 900°C.

In Fig. 2 are shown room temperature Er^{3+} PL spectra for the Er-implanted GaN samples using above-bandgap excitation from the UV-lines of an Ar ion laser (336–363 nm). As with below-bandgap excitation, no PL signal was detected in the as-implanted sample. After annealing at 800°C, there was a broad PL signal centered at ~ 1530 nm. The intensity of the PL spectrum increased with annealing at higher temperatures and became more indicative of the transition between the $^4I_{13/2}$ and the $^4I_{15/2}$ manifolds. The PL signal reached a maximum after annealing at 1050°C and a detectable Er^{3+} PL signal was present even after annealing at 1100°C.

The PL spectra shown in Fig. 2 may be due to a different set of Er^{3+} complexes than the ones leading to the spectra shown in Fig. 1. Since above-bandgap excitation produces a large number of electron-hole pairs, it is possible that several different Er^{3+} complexes may be excited in the process. However, the implantation-induced damage reduces the generation rate of electron-hole pairs and provides non-radiative recombination channels. Consequently, the optimum annealing temperature for above-bandgap excitation is likely to be different than that for below-bandgap excitation and the spectra are likely to differ. Again, some minimum annealing temperature may be required to reduce the damage-related absorption to low enough levels to permit detection of the Er^{3+} PL spectra.

3.2. Bandedge luminescence

In Fig. 3 are shown the bandedge PL spectra for the GaN samples, measured at 10 K and at RT, over the range of 3.0 eV (410 nm)–3.7 eV (333 nm). The excitation source for these measurements was a laser at a wavelength of 290 nm. As shown in Fig. 3a, the unimplanted GaN sample has a well-defined PL peak at

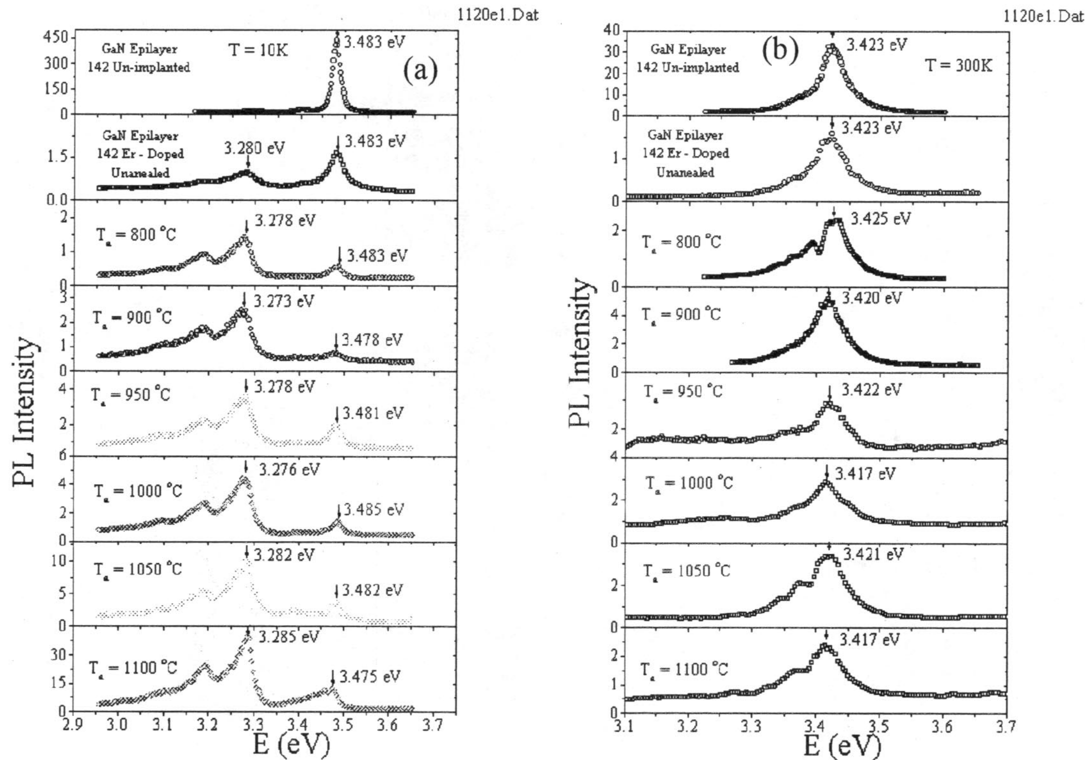

Fig. 3. Bandedge PL spectra of Er-implanted GaN as a function of annealing temperature. The samples were excited using a laser source at a wavelength of 290 nm: (a) spectra measured at 10 K; (b) spectra measured at room temperature.

3.483 eV (354 nm) with a FWHM of 20 meV, when measured at 10 K. After co-implantation with Er and O ions, the bandedge PL peak is still detectable even though its intensity is significantly reduced. In addition, another PL peak can be observed at ~ 3.280 eV (376 nm). This PL peak seems to be related to the co-implantation of Er and O ions. There is a further PL peak at 3.180 eV (388 nm) that can be detected with annealing at temperatures above 800°C. This peak appears to be a phonon replica of the peak at 3.280 eV observed in the unannealed sample. The intensity of both of these PL peaks increases with annealing. However, as shown in Fig. 4, the intensity of the peak at ~ 3.278 eV Fig. 4(a), increases faster than that of the bandedge transition, Fig. 4(b). After annealing at 1100°C, the intensity of the peak at 3.278 eV is nearly four times greater than that of the bandedge.

As shown in Fig. 3b, the PL measurements taken at RT exhibit a similar behavior. In the unimplanted GaN sample, the bandegde peak shifted to 3.423 eV (360 nm) and broadened to a FWHM of 40 meV. After co-implantation, the intensity of the bandedge peak was significantly reduced. However, no PL peak at ~ 3.220 eV (383 nm) can be observed. With annealing, the intensity of the bandedge peak remains nearly constant but its FWHM increases.

With above-bandgap excitation of the Er^{3+} ions, the GaN bandedge emission lines may provide effective radiative recombination channels that reduce the excitation efficiency of intra-4f transitions. Some of the electron-hole pairs that are produced with above

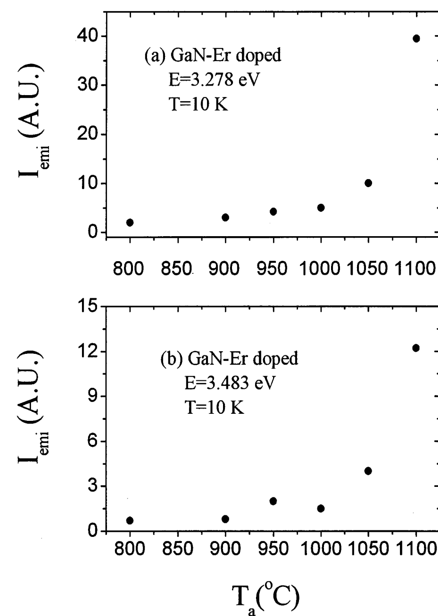

Fig. 4. Intensity of the bandedge PL peaks, measured at 10 K, of Er-implanted GaN as a function of annealing temperature. The samples were excited using a laser source at a wavelength of 290 nm: (a) intensity of the peak at 3.278 eV; and (b) intensity of the peak at 3.483 eV.

bandgap excitation may recombine to produce luminescence at ~ 3.42 eV instead of transferring energy to the Er^{3+} complexes that result in the spectra shown in Fig. 2.

SIMS analysis indicated that the Er atomic profile is unchanged even after annealing at 1100°C. However, annealing in a N ambient at temperatures above 900°C does lead to high concentrations of O and C being introduced into the film. The reduction in the Er^{3+} PL signal after high temperature annealing may be related to changes in composition of the GaN matrix.

4. Summary

Ion implantation is a convenient method for doping GaN semiconductor films with Er atoms. However, Er implantation causes considerable damage to the GaN crystal. Co-implantation with O ions increases the damage and high temperature post-implantation annealing is required to observe Er^{3+} photoluminescence. After Er and O ion implantation, an optical transition at ~ 3.28 eV appears in the PL spectrum. The intensity of both this peak and the bandedge emission increases monotonically with annealing up to 1100°C.

The Er^{3+} PL near 1540 nm was detectable at RT only after annealing at 800°C. With below-bandgap excitation, the intensity of the Er^{3+} PL reached a maximum with annealing at 900°C. Annealing at higher temperatures resulted in a diminished PL signal. With above-bandgap excitation, the intensity of the Er^{3+} PL reached a maximum with annealing at 1050°C. Based on SIMS analysis, the Er atomic profile is unchanged even after annealing at such high temperatures. However, annealing in N ambient at temperatures above 900°C resulted in high concentrations of O and C in the film. This change in composition of the GaN matrix may be responsible for the diminished PL signals after high temperature annealing.

Acknowledgements

The authors wish to acknowledge the US Army Research Office for support of this research.

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.T. Torvik, R.J. Feuerstein, C.H. Qui, M.W. Leksono, F. Namavar, J.I. Pankove, Mat. Res. Soc. Symp. Proc. 422 (1996) 199–204.
[3] S. Kim, S.J. Rhee, D.A. Turnbull, E.E. Reuter, X. Li, J.J. Coleman, S.G. Bishop, Appl. Phys. Lett. 71 (1997) 231–233.
[4] H.J. Lozykowski, W.D. Jadwisinczak, I. Brown, Appl. Phys. Lett. 74 (1999) 1129–1132.
[5] P.N. Favennec, H. L'Haridon, D. Moutonnet, M. Salvi, M. Gauneau, Jpn. J. Appl. Phys. 29 (4) (1990) L524–526.
[6] J. Michel, J.L. Benton, R.F. Ferrante, D.C. Jacobson, D.J. Eaglesham, E.A. Fitzgerald, Y. Xie, J.M. Poate, L.C. Kimerling, J. Appl. Phys. 70 (5) (1991) 2672–2678.
[7] J.E. Colon, D.W. Elsaesser, Y.K. Yeo, R.L. Hengehold, G.S. Pomrenke, Mat. Res. Soc. Symp. Proc. 301 (1993) 169–174.
[8] R.G. Wilson, F.A. Stevie, C.M. Magee, Secondary Ion Mass Spectrometry: A Practical Guide for Depth Profiling and Bulk Impurity Analysis, Wiley, New York, 1989.
[9] E. Alves, M.F. DaSilva, J.C. Soares, J. Bartels, R. Vianden, C.R. Abernathy, S.J. Pearton, MRS Internet J. Nitride Semicond. Res. 4S1 (1999) G11.2. See also article 3.1 in this issue.
[10] J.T. Torvik, C.H. Qui, R.J. Feuerstein, J.I. Pankove, F. Namavar, J. Appl. Phys. 81 (1997) 6343.
[11] R. Dupuis, J. Crystal Growth 178 (1997) 56.
[12] M. Thaik, U. Hömmerich, R.N. Schwartz, R.G. Wilson, J.M. Zavada, Appl. Phys. Lett. 71 (1997) 2641–2643.
[13] S. Kim, S.J. Rhee, J.O. White, A.M. Mitofsky, X.Li, G.C. Papen, J.J. Coleman and S.G. Bishop, MSB 81 (2001).