Site-selective Photoluminescence Spectroscopy of Er-implanted Wurtzite GaN under Various Annealing Condition

Sangsig Kim*, Man Young Sung, and Jinki Hong
Department of Electrical Engineering, Korea University, Seoul 136-701, Korea

Moon-Sook Lee
Semiconductor R&D Center, Samsung Electronics, Co. Ltd, Korea

E-mail : sangsig@kuccnx.korea.ac.kr

(Received 16 February 2000, Accepted 24 March 2000)

The ~1540 nm $^4I_{13/2} \rightarrow {}^4I_{15/2}$ emissions of Er^{3+} in Er-implanted GaN annealed at temperatures in the 400 to 1000 °C range were investigated to gain a better understanding of the formation and dissociation processes of the various Er^{3+} sites and the recovery of damage caused by the implantation with increasing annealing temperature (T_A). The monotonic increase in the intensity of the broad defect photoluminescence (PL) bands with increasing T_A proves that these are stable radiative recombination centers introduced by the implantation and annealing process. These centers cannot be attributed to implantation-induced damage that is removed by post-implantation annealing. Selective wavelength pumping of PL spectra at 6 K reveals the existence of at least nine different Er^{3+} sites in this Er-implanted semiconductor. Most of these Er^{3+} PL centers are attributed to complexes of Er atoms with defects and impurities which are thermally activated at different T_A . Only one of the nine observed Er^{3+} PL centers can be pumped by direct 4f absorption and this indicates that it is the highest concentration Er^{3+} center and it represents most of the optically active Er^{3+} in the implanted sample. The fact that this Er^{3+} center cannot be strongly pumped by above-gap light or broad band below-gap absorption indicates that it is an isolated center, i.e. not complexed with defects or impurities. This *4f*-pumped PL spectrum appears at annealing temperatures as low as 400 °C, and although its intensity increases monotonically with increasing T_A, the wavelengths and linewidths of its characteristic peaks are unaltered. The observation of this high quality Er^{3+} PL spectrum at low annealing temperatures illustrates that the crystalline structure of GaN is not rendered amorphous by the ion implantation. The increase of the PL intensities of the various Er^{3+} sites with increasing T_A is due to the removal of competing nonradiative channels with annealing.

Keywords : photoluminescence, Er-implanted GaN, annealing, Er^{3+} center

1. INTRODUCTION

Our previous site-selective photoluminescence (PL) and photoluminescence excitation (PLE) spectroscopies carried out on the ~1540 nm $^4I_{13/2} \rightarrow {}^4I_{15/2}$ emissions of Er^{3+} in Er-implanted GaN revealed the existence of four different Er^{3+} sites in this semiconductor annealed at a temperature of 900 °C [1-3]. The four different Er^{3+} sites existing in this Er-implanted GaN can be separately and selectively excited by three different below-gap optical absorption processes [4]: 1) unidentified, impurity- or defect-related absorption bands, 2) an absorption band associated with an Er-related defect or trap, 3) and direct, sharp-line Er^{3+} intra-*4f* shell absorption bands. The first two excitation processes involve trap-mediated mechanisms in which absorption by the defects or impurities is followed by efficient, nonradiative transfer of the excitation energy to neighboring Er^{3+} sites. In this annealing study, the formation and dissociation processes of these four Er^{3+} sites with increasing annealing temperature (T_A) are investigated, and new Er^{3+} sites formed under different annealing conditions are revealed.

In this study, PL spectroscopy has explored the effects

of a range of T_A on the activation of the multiple Er^{3+} centers and their emission efficiencies under selective excitation by below-gap absorption mechanisms. The goal of this study is to examine the formation and dissociation processes of the various Er^{3+} sites with increasing T_A, the origin of the broad defect PL bands, and how the recovery with increasing T_A of the ion implantation damage in GaN affects the PL of multiple Er^{3+} centers.

2. EXPERIMENTAL PROCEDURE

The GaN films were grown on sapphire by atmospheric pressure MOCVD, and were implanted with a dosage of 4×10^{13} Er ions/cm^2 at 280 keV [1-3]. The implanted sample was annealed in a conventional tube furnace at temperatures ranging from 400 to 1000 °C for 90 minutes under a continuous flow of nitrogen gas [5].

6K PL spectroscopy was carried out on the Er-implanted GaN annealed at seven different temperatures in the 400 to 1000 °C range. The PL spectra were excited by a variety of sources including a tunable titanium-doped sapphire laser, a HeNe laser, an Ar ion laser, a Xe lamp dispersed by a double grating monochromator, and a HeCd laser. After finishing a complete set of PL experiments in the sample annealed at lower temperature, the same sample was annealed at higher temperature. The luminescence was analyzed by a 1-m single grating monochromator and detected by a cooled Ge PIN detector. Samples were cooled to liquid helium temperature in a Janis Supervaritemp Cryostat.

3. RESULTS AND DISCUSSION

Figure 1 shows the 6K PL spectra in the ~ 0.73 - 1.2 eV spectral range obtained from an Er-implanted film of GaN annealed at temperatures in the 400 to 1000 °C range. All the PL spectra excited by 515 nm light exhibit the sharply structured 1540 nm band characteristic of the $^4I_{13/2} \rightarrow {}^4I_{15/2}$ transitions of Er^{3+} and the broad defect PL bands peaking at 1200 and 1270 nm on which the Er-related PL band is superimposed [1]. The 515 nm pumping line is marked by an arrow on the strong absorption band peaking at 2.35 eV in the PLE spectrum (Fig. 2a) detected at the ~1.04 eV peak position of the highest intensity in the broad-band damage-induced emission in the sample annealed at 900 °C in Fig. 1. The 2.35 eV PLE band in this PLE spectra appears to excite a mixture of some Er^{3+} PL spectra from Er^{3+}-defect or -impurity complex sites as well as the damage-induced broad-band PL [4]. The excitation of some Er^{3+}-defect complex PL spectra (see Fig. 3) by

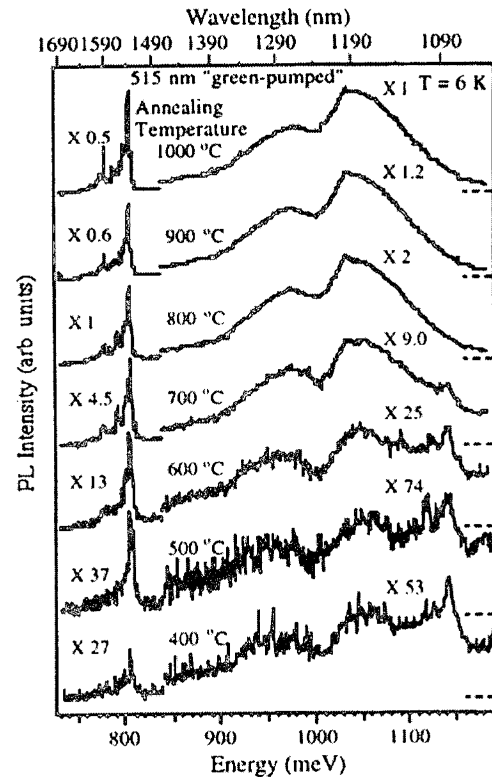

Fig. 1. The Er^{3+} PL spectra and the broad defect PL bands (pumped by 515 nm light).

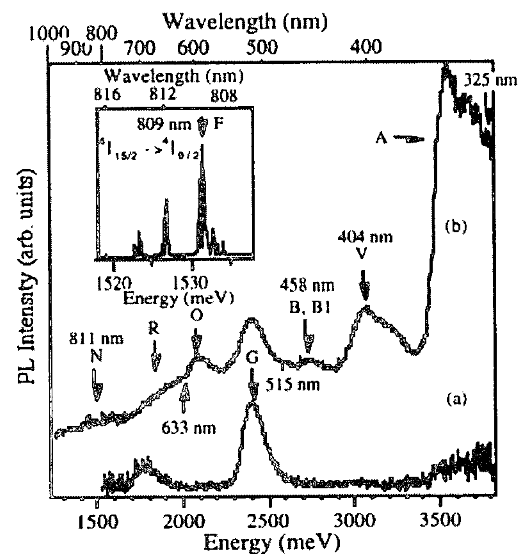

Fig. 2. The PLE spectra showing absorption bands associated with Er^{3+} centers and damage-induced defects.

pumping light within this band is due to the overlapping of some broad PLE bands (shown in Fig. 2b) which selectively excite these Er^{3+} PL spectra.

The broad defect PL bands seen in the PL spectra of the sample annealed at temperatures higher than 600 °C

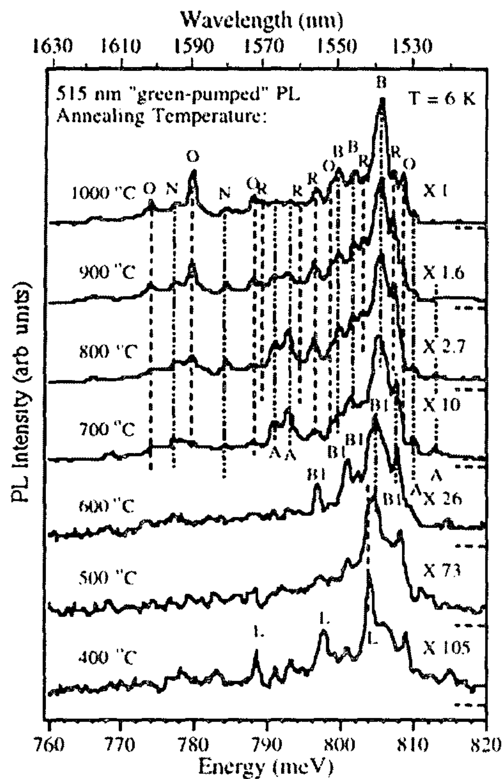

Fig. 3. The Er^{3+} PL spectra pumped by 515 nm light.

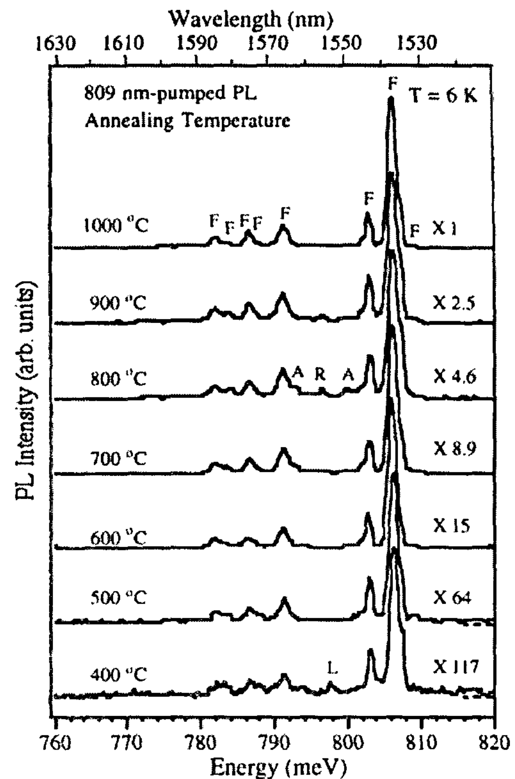

Fig. 4. The Er^{3+} PL spectra pumped by 809 nm light.

(Fig. 1) were suggested previously to be related to ion-implantation induced damage [1,4]. This assignment was based on the observations that the PL spectrum from Cr- (or Nd-) implanted samples' of the same GaN film annealed at 900 °C (or 1000 °C) for 30 minutes shows the same broad defect PL band as obtained from an Er-implanted sample annealed under the same annealing condition [1] and that these defect PL bands are not seen in unimplanted samples annealed under the same annealing condition. Nearly identical defect PL bands were also reported by Silkowski *et al.* for Er- and Nd-implanted films of GaN annealed at 1000 °C [5,6]. The careful annealing studies presented here show that the broad damage-induced PL is not observed in the unannealed sample, is weakly observed in the sample annealed at 400 and 500 °C, and gets stronger in intensity as T_A is raised to 1000 °C. These observations indicate that the defects responsible for these broad PL bands are not directly induced by the implantation process, but are thermally activated with increasing T_A as the crystal recovers gradually from its damaged state. The monotonic increase in the intensity of the broad band PL with increasing T_A proves that these are stable radiative recombination centers introduced by the implantation and annealing process. These defects cannot be characterized as implantation-induced damage that is *removed* as crystalline quality is restored by post-implantation annealing.

The annealing study presented here reveals nine distinct optically active Er^{3+} centers using excitation wavelength and annealing conditions (in the 400 to 1000 °C range) that separately optimized each PL spectrum. Notice that there are no Er^{3+} PL emissions from the unannealed sample excited by below-gap light (all nine sites are optically inactive in the unannealed sample). The detailed site-selective PL spectra associated with all nine distinct optically active Er^{3+} centers are not shown here because of limited space. However, the ~1540 nm Er^{3+} PL spectra in Fig. 3 for all T_A in the 400 to 1000 °C range as excited by 515 nm light show still seven out of nine distinct optically a ctive Er^{3+} centers; the PL peaks associated with the Er^{3+} centers labeled above-gap (A), blue (B), new-blue (B1), orange (O), red (R), near-IR (N), and low temperature (L) are seen in the 515 nm-pumped PL spectra, while the PL peaks due to two other Er^{3+} centers labeled 4*f* (F) and violet (V) are absent. In most cases the labels for the PL spectra are based on the pump wavelengths used to selectively excite the various Er^{3+}centers. The excitation of the seven defect-associated Er^{3+} PL spectra in Fig. 3 is due to the overlapping of some broad absorption bands (which selectively excite these respective Er^{3+} PL spectra) at 515 nm. The absorption bands with labels corresponding to those of the associated PL peaks are all superimposed in the broad band PLE spectrum (shown in Fig. 2b) which was obtained by detecting the integrated Er^{3+} PL from all of

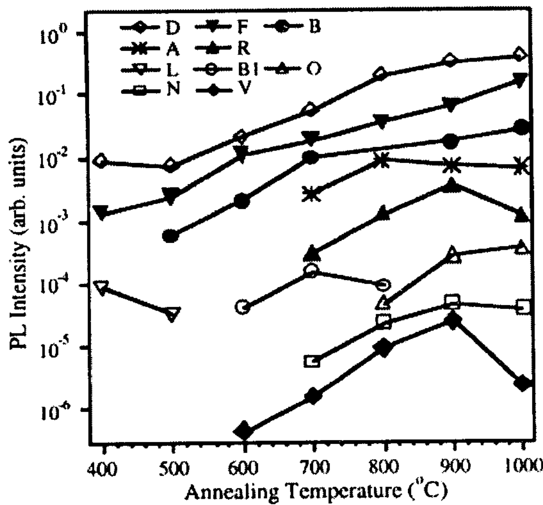

Fig. 5. Dependence upon T_A of the PL intensity of the distinct PL peaks.

the different Er^{3+} sites [1]. The ~810 nm high resolution PLE spectrum shown in the inset to Fig. 2 was obtained with the tunable Ti:sapphire laser [3]. It exhibits the sharp $^4I_{15/2} \rightarrow {}^4I_{9/2}$ $4f$ absorption lines expected for a single Er^{3+} site. Correspondingly, resonant excitation at any of these sharp lines pumps the PL spectrum associated with the $4f$-pumped (F) site (see Fig. 4). In Fig. 5, the peak intensities of the distinct PL spectra associated with nine different optically active Er^{3+} centers are plotted as a function of T_A. The various annealing curves have been arbitrarily displaced in the vertical dimension for clarity of presentation. The dependence upon T_A of the integrated intensity (labeled D) for the damage-induced PL spectrum is also compared in Fig. 5 with the peak intensities associated with nine distinct optically active Er^{3+} centers. The data of Fig. 5 provide two insights concerning the formation of the distinct Er^{3+} centers in Er-implanted and annealed GaN. First, the high concentration center pumped by direct Er^{3+} $4f$-shell absorption is activated at the lowest T_A investigated, 400 °C. Second, the PL intensities of all the Er^{3+} centers increase as a function of T_A with approximately the same rates from their respective activation temperatures until they either saturate or begin to decrease. Furthermore, the rate of increase of the PL intensities of the Er^{3+} centers with increasing T_A (above 600 °C) closely parallels that of the broad defect-related PL bands. This indicates that the increase in the PL efficiencies of the Er^{3+} centers with increasing T_A is attributable primarily to the progressive removal of competing non-radiative recombination centers, and not to the activation of increasing numbers of the various centers [7].

Figure 4 shows the strong PL peaks associated with the F site excitable by direct Er^{3+} $4f$-shell absorption. The observation of this particular spectrum, its optical excitation properties, and its response to the annealing process enable us to draw several conclusions regarding the incorporation of implanted Er in the GaN lattice. First, the fact that this is the only Er^{3+} PL center of the nine observed that can be pumped by direct $4f$ absorption indicates that it represents most of the optically active Er^{3+} in the implanted sample [3,4]. Second, the fact that it is strongly pumped only by the sharp-line $4f$ band absorption (it is pumped only weakly by above gap light and exhibits no broad-band, below-gap PLE) indicates that this center is isolated, i.e. not complexed with defects or impurities [3,4]. Third, this PL spectrum is observed in Er-implanted GaN annealed at temperatures as low as 400 °C, and the wavelengths and line widths of the high quality, sharpline spectrum shown in Fig. 4 do not change with increasing T_A. This indicates that most of the Er at`oms are on identical, high-quality sites in the GaN, since there is no evidence of disorder- or damage-induced site-to-site variations in the crystal field that would cause spectral broadening of the Er^{3+} emission spectrum. This is in striking contrast to in situ Er-doped GaN and AlN for which the Er^{3+} emission spectra are severely broadened and exhibit none of the fine structure characteristic of the Er^{3+} PL spectra from Er-implanted and annealed GaN samples [8,9].

The dependence upon T_A of the integrated intensity for the F center PL spectrum is compared with that of the integrated PL intensity for the damage-induced PL spectrum in Fig. 5. The $4f$-pumped PL intensity (on a log scale) increases monotonically with T_A. This observation leads to a fourth suggestion that, for T_A ranging from 400 to 1000 °C, a single thermally activated process is responsible for annealing much of the implantation damage associated with nonradiative recombination centers that compete with the $4f$-pumped PL. The intensity of the damage-induced PL spectrum follows a roughly similar behavior over the same T_A range. These observations are consistent with the recent results reported by Dalmer *et al.* [10] and Ronning *et al.* [11] concerning the effects of annealing on the sites of implanted ions and on the damage induced by the implantation. Dalmer *et al.* showed that, in unannealed GaN implanted with ^{167}Tm, rare earth atoms occupy relaxed substitutional (Ga) lattice sites and that isochronal annealing treatments up to 800 °C do not influence the lattice sites of the rare earth elements [10]. Ronning *et al.* showed that, in unannealed GaN implanted with ^{111}In, 90 percent of the indium atoms occupy substitutional (Ga) lattice sites within a heavily disturbed surrounding, that a gradual recovery of the implantation damage in the environment of the indium atoms takes place between 600 and 900 °C, and that, for T_A higher than 900 °C, about 50 % of the In atoms occupy substitutional lattice (Ga) sites with defect free

surroundings and other In atoms occupy substitutional sites with weakly disturbed surroundings [11]. These studies demonstrate that the crystalline structure of GaN is not significantly destroyed by the ion implantation and that the created damage can be annealed out to a large extent.

These findings may also apply to the annealed sample in the current study since the implantation conditions used by Dalmer *et al.* and Ronning *et al.* [10,11] are very close to ours. Their results are consistent with our observation that, the 4*f*-pumped Er^{3+} PL spectrum exhibits a high quality, sharpline spectrum even at the lowest annealing temperature employed, and its spectral characteristics are not altered with increasing T_A. The increase of the PL intensity in the 4*f*-pumped spectrum is not likely to be related to the increase in the number of the F centers, since most implanted Er^{3+} ions presumably occupy substitutional lattice (Ga) sites even in the unannealed sample and their number is not changed with annealing. Its increase is more likely due to the removal of nonradiative channels with annealing.

4. CONCLUSIONS

Site selective PL studies of Er-implanted GaN annealed at temperatures in the range 400 to 1000 °C reveal the existence of nine different Er^{3+} sites. Eight of these Er^{3+} PL centers are attributed to complexes of Er atoms with defects and impurities which are thermally activated at different T_A. Only one of the nine observed Er^{3+} PL centers can be pumped by direct 4*f* absorption and this indicates that it is the highest concentration Er^{3+} center. On the basis of its excitation characteristics, it is concluded that this 4*f*-pumped center is an isolated center and it represents most of the optically active Er^{3+} in the implanted sample. The high spectral quality of the 4*f*-pumped PL spectrum at all T_A (even as low as 400 °C) illustrates that the crystalline structure of GaN is not rendered amorphous by the ion implantation. The observed increase of the PL intensities of the various Er^{3+} sites with increasing T_A is attributed to the removal of competing nonradiative channels with annealing. A parallel monotonic increase with increasing T_A in the intensity of the broad defect PL bands peaking proves that these are stable radiative recombination centers introduced by the implantation and annealing process. These centers cannot be attributed to implantation-induced damage that is removed by post-implantation annealing.

ACKNOWLEDGMENTS

This study was supported by the special research fund of Korea University and the loan program (for new appointed professors) of Research Institute for Information & Communication Technology

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