PHOTOLUMINESCENCE AND PHOTOLUMINESCENCE EXCITATION SPECTROSCOPY OF *IN SITU* Er-DOPED AND Er-IMPLANTED GaN FILMS GROWN BY HYDRIDE VAPOR PHASE EPITAXY

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ABSTRACT

Photoluminescence (PL) and photoluminescence excitation (PLE) spectroscopy have been carried out at 6K on the 1540 nm $^4I_{13/2}$ $^4I_{15/2}$ emission of Er^{3+} in *in situ* Er-doped and Er-implanted GaN grown by hydride vapor phase epitaxy (HVPE). The PL and PLE of these two different Er-doped HVPE-grown GaN films are compared with Er-implanted GaN grown by metal organic chemical vapor deposition (MOCVD).

In the *in situ* Er-doped HVPE-grown GaN, the lineshape of the broad PLE absorption bands and the broad PL bands is similar to that in Er-doped glass. The PL spectra of this *in situ* Er-doped sample are independent of excitation wavelength, unlike the PL of the Er-implanted GaN. These PL spectra are quite different from the site-selective PL spectra observed in the Er-implanted GaN, indicating that the seven different Er^{3+} sites existing in the Er-implanted MOCVD-grown GaN are not observed in the *in situ* Er-doped HVPE-grown GaN. Four of the seven different Er^{3+} sites observed in the Er-implanted MOCVD-grown GaN annealed at 900 ^oC under a flow of N_2 are present in the Er-implanted HVPE-grown GaN annealed at 800 ^oC in an NH_3/H_2 atmosphere.

INTRODUCTION

Photoluminescence (PL) and photoluminescence excitation (PLE) spectroscopy have been performed to study the different structural configurations (sites or centers) on which Er^{3+} ions are incorporated in Er-doped GaN and to investigate their excitation mechanisms [1-7]. Our previous study of site-selective PL and PLE spectroscopy in Er-implanted samples of GaN grown by metal organic chemical vapor deposition (MOCVD) that were annealed at 900 ^oC under a flow of N_2 revealed the existence of seven different Er^{3+} sites [3]. Six of these Er^{3+} PL sites are attributed to complexes of Er atoms with defects and impurities. Only one of the seven sites can be pumped by direct 4*f* absorption; the concentrations of the other sites are too low to allow excitation by direct 4*f* absorption. These results raise an obvious question concerning the generality or uniqueness of the Er^{3+} centers observed in GaN. That is, are these multiple, selectively excited, discrete Er^{3+} sites or centers unique to Er-implanted MOCVD-grown GaN subjected to specific post-implantation annealing conditions, or are they also present in Er-doped GaN synthesized by other growth, doping and annealing procedures?

Site-selective PL and PLE spectroscopies used in our previous work are applied in this study to Er-implanted hydride vapor phase epitaxy (HVPE)-grown GaN annealed at 800 ^oC in an NH_3/H_2 atmosphere and *in situ* Er-doped HVPE-grown GaN [7] to see if any of the seven

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different Er^{3+} sites observed in Er-implanted MOCVD-grown GaN exist in these samples. The PLE and PL of these two different HVPE-grown samples are compared here first with the Er-implanted MOCVD-grown sample and then the differences and similarities among the site-selective PLE and PL spectra of these three different Er-doped GaN films are discussed in detail.

EXPERIMENTAL PROCEDURE

The GaN films were doped *in-situ* with Er in a horizontal HVPE reactor during growth. A peak Er concentration of 2×10^{19} ions/cm^3 was achieved in this *in situ* Er-doped GaN at a thickness of 1000 nm [7]. The GaN films grown on sapphire by HVPE were implanted with a dosage of 2×10^{14} ions/cm^2 at 300 keV. The peak concentration of Er is 5.3×10^{19} ions/cm^3 at a depth of 33 nm [7]. These Er-implanted HVPE-grown GaN films were annealed in a conventional tube furnace at 800 ^{o}C for 30 minutes in a flowing NH_3/H_2. For comparison, the GaN films grown on sapphire by atmospheric pressure MOCVD were implanted with a dosage of 4×10^{13} ions/cm^2 at 280 keV [1-4]. The peak concentration of Er is 2×10^{18} ions/cm^3. Post-implantation annealing was carried out in a conventional tube furnace at 900 ^{o}C for 30 minutes under a continuous flow of nitrogen gas.

6K PL spectroscopy was carried out on the three different Er-doped GaN samples. 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. The PLE spectra were obtained with a xenon lamp dispersed by a double grating monochromator or with a tunable titanium-doped sapphire laser. All of the PLE spectra were corrected for the spectral response of the tunable excitation systems. 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.

RESULTS AND DISCUSSION

Figure 1 shows the PL spectra obtained at 6 K under excitation by 515 nm light ("green-pumped") from *in situ* Er-doped and Er-implanted GaN grown by HVPE. The PL spectrum taken for Er-implanted MOCVD-grown GaN under the same experimental conditions is also shown for comparison. All three PL spectra exhibit the 1540 nm band characteristic of the $^4I_{13/2}$ $^4I_{15/2}$ transitions of Er^{3+} and broad background PL bands on which the Er-related PL bands are superimposed. In the PL of the *in situ* Er-doped GaN (Fig. 1a), the broad PL bands have different lineshapes and peak positions from those of the damage-induced broad-band PL observed in the Er-implanted MOCVD-grown GaN (Fig. 1c) [4]. Since these bands have not been observed in

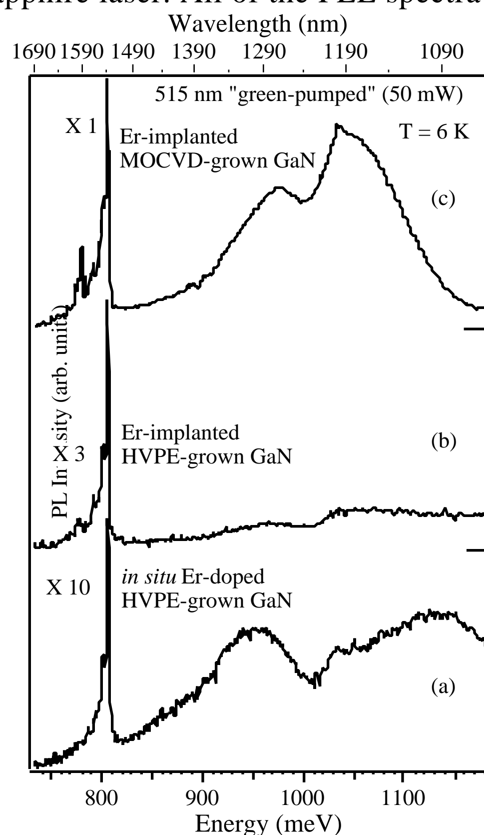

Fig. 1. The Er^{3+} PL spectra and the broad defect PL bands (pumped by 515 nm light).

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undoped HVPE-grown GaN, they are apparently induced by the *in situ* doping during growth. In the PL spectrum of the Er-implanted HVPE-grown GaN (Fig. 1b), the damage-induced broad-band PL is barely observable.

Figure 2 displays the PLE spectra of the three different Er-doped samples obtained by detecting the integrated Er^{3+} PL intensity while scanning the wavelength of the xenon lamp-double monochromator excitation system. The PLE spectrum 2(a) of the *in situ* Er-doped sample exhibits relatively narrow absorption bands attributable to direct optical excitation of the intra 4*f*-shell transitions of Er^{3+}, and an exponential absorption tail just below the 3.5 eV band gap. The exponential energy dependence of the below-gap absorption tail is reminiscent of the Urbach absorption edge that characterizes the band edge of disordered materials such as chalcogenide glasses [8] or highly doped crystalline semiconductors [9]. This PLE spectrum does not show the broad, mid-gap defect- or impurity-related absorption bands that are observed in the PLE spectra 2(b) and 2(c) of the Er-implanted samples. The absorption peaks seen at 378, 400, 445, 487, 521, 543, 651, 796, and 970 nm in the PLE spectrum 2(a) are attributed to $^4I_{15/2}$ $^4G_{11/2}$, $^4I_{15/2}$ $^4H_{9/2}$, $^4I_{15/2}$ $^4F_{3/2,5/2}$, $^4I_{15/2}$ $^4F_{7/2}$, $^4I_{15/2}$ $^4H_{11/2}$, $^4I_{15/2}$ $^4S_{5/2}$, $^4I_{15/2}$ $^4F_{9/2}$, $^4I_{15/2}$ $^4I_{9/2}$, and $^4I_{15/2}$ $^4I_{11/2}$ Er^{3+} intra 4*f*-shell transitions, respectively [5,6,10]; some of these PLE bands were reported in Refs. 5 and 6 to be observed in Er-implanted GaN and *in situ* Er-doped AlN grown by molecular-beam epitaxy (MBE). In contrast, the PLE spectra 2(b) and 2(c) obtained from the Er-implanted HVPE- and MOCVD-grown samples, respectively, show only the broad, defect- or impurity-related absorption bands that are not attributable to Er^{3+}. These absorption bands are characteristic of the implanted films only, suggesting that some of the broad absorption bands in the PLE spectra 2(b) and 2(c) are associated with defects or defect-impurity complexes created during the implantation and annealing procedures [1,3].

The high-resolution PLE spectra (Fig. 3) obtained in the 775-825 nm spectra range with

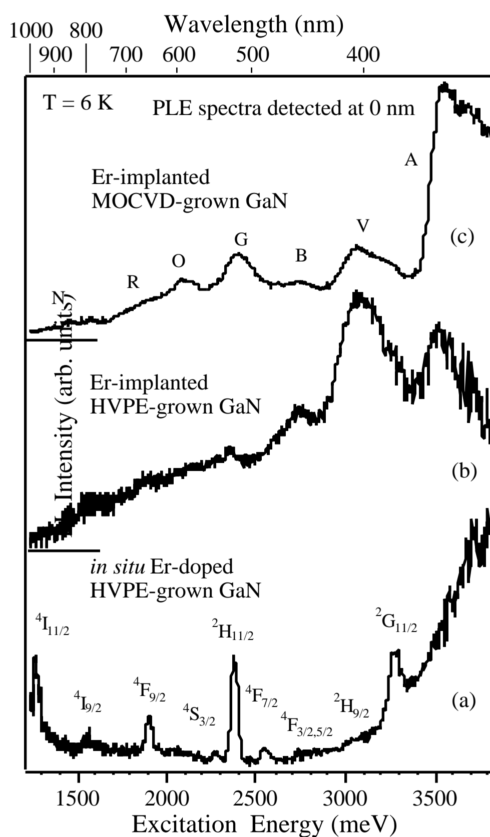

Fig. 2. The PLE spectra obtained by detecting the integrated Er^{3+} PL intensity.

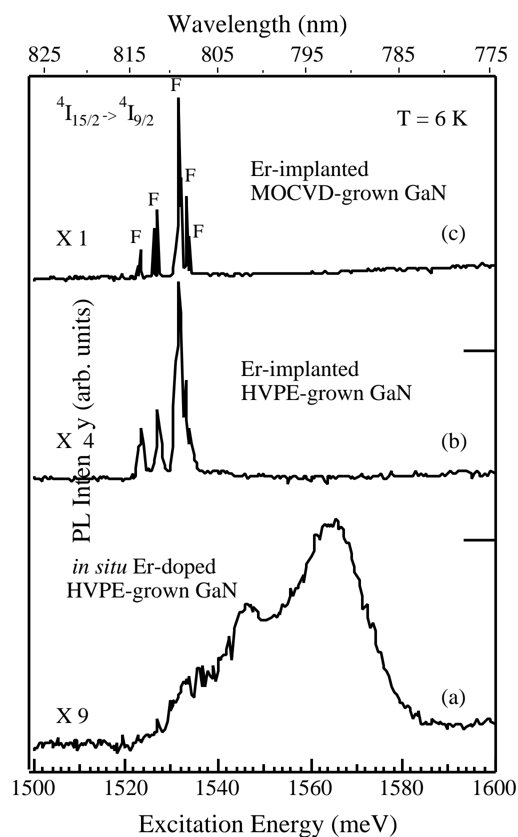

Fig. 3. The $^4I_{15/2}$ $^4I_{9/2}$ 4*f* shell Er^{3+} PLE spectra.

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the tunable Ti-doped sapphire laser exhibit PLE peaks assigned to direct ${}^4I_{15/2}$ ${}^4I_{9/2}$ 4*f* shell absorption. The absorption bands seen in the PLE spectrum (Fig. 3a) of the *in situ* Er-doped sample are much broader and their peak positions are shifted to the shorter wavelength region, compared to the Er-implanted samples. Note that the PLE spectrum of the MOCVD-grown GaN in Fig. 3c shows five pairs of sharp peaks, indicative of a single type of Er^{3+} center or site. The loss of the sharp structure in the PLE spectrum of the *in-situ* Er-doped GaN sample indicates that the Er dopants in this sample occupy sites located in disordered regions of the material. The disordered or "amorphous" character of the Er^{3+} centers' structural environments gives rise to site-to-site variations in the magnitude and symmetry of the crystal fields experienced by the Er^{3+} ions that are responsible for the spectral broadening of the Er^{3+} 4*f* PLE bands [8,9]. Additional evidence for disorder in the structural environment of the Er dopants in the GaN doped during growth is provided by the broad Urbach absorption edge in the near-band edge PLE spectrum of Fig. 2a, which contrasts strongly with the relatively sharp band edge absorption features observed in the PLE spectra of the Er^{3+} emission in Er-implanted samples of GaN (see, for example, Fig. 2c). Furthermore, the 1540 nm Er^{3+} PL bands from the *in situ* Er-doped sample shown in Figs. 1a, 5a, and 7a all have a broadened line shape more characteristic of Er dopants in glasses [8], than the sharply structured 1540 nm Er^{3+} PL bands of the Er-implanted GaN samples shown in Figs. 1b and c, 5b and c, 6a and b, and 7b and c.

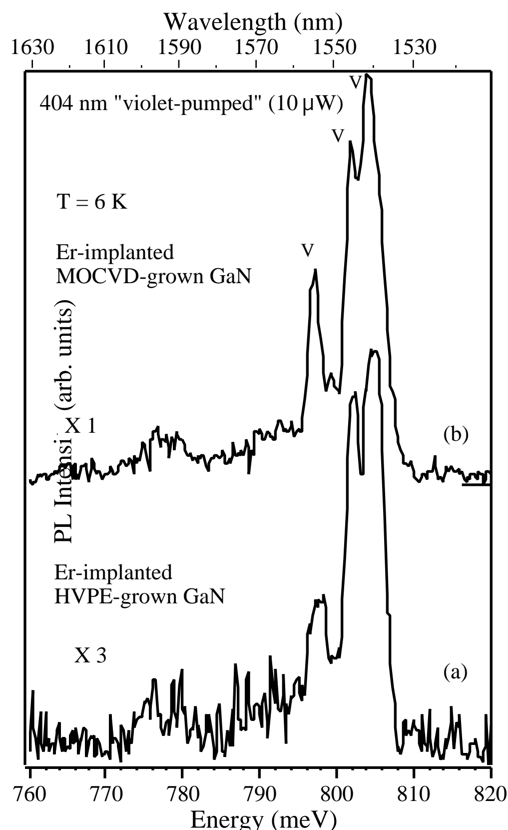

Fig. 4. The “violet-pumped” PL spectra as excited by violet light (404 nm).

The PLE spectrum of the Er-implanted HVPE-grown GaN in Fig. 3b exhibits sharp-structured peaks having the same peak positions as those in the Er-implanted MOCVD-grown GaN (Fig. 3c). A careful comparison between these two PLE absorption bands reveals that the PLE peaks in the HVPE-grown one are broader, compared to the MOCVD-grown one. The broadening of the sharp ${}^4I_{15/2}$ ${}^4I_{9/2}$ 4*f* shell absorption peaks in the Er-implanted, HVPE-grown sample is apparently attributable to the fact that the concentration (5.3 x 10^{19} ions/cm^3) of the implanted Er^{3+} ions is larger than that (2 x 10^{18} ions/cm^3) in the Er-implanted MOCVD-grown sample; a similar broadening of the sharp absorption peaks was observed in the PLE spectrum of MOCVD-grown GaN implanted with 10^{15} Er ions/cm^2 at 350 keV reported in Ref. 11. While the sharpness of the PLE peaks in the PLE spectrum of the Er-implanted MOCVD-grown GaN indicates that isolated Er ions on Ga atomic positions are on identical, high-quality sites in this material [4], the spectral broadening of the direct 4*f* PLE absorption peaks for the Er-implanted HVPE-grown sample implies moderate site-to-site variation in the crystal field.

The seven distinct optically active Er^{3+} centers observed previously in the Er-implanted MOCVD-grown GaN annealed at 900 ^{o}C (Ref. 3) have been labeled on the basis of their excitation wavelengths, as follows: above-gap (A), blue (B), orange (O), red (R), near-IR (N), 4*f*

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(F) and violet (V). This labeling system has been used to identify the PLE absorption bands associated with the selective excitation of these Er^{3+} centers in the PLE spectra in Figs. 2c and 3c. Figures 4, 5, and 6 show the "violet-pumped", "blue-pumped", and "red-pumped" PL spectra excited by 404, 458 and 633 nm light, respectively, that correspond with the similarly labeled PLE bands in Fig. 2c [4]. The "violet-pumped" PL spectra presented in Fig. 4 demonstrate that the PL peaks in the "violet-pumped" PL spectrum of the Er-implanted HVPE-grown GaN are the same as those in the Er-implanted MOCVD-grown GaN, while there was no Er^{3+} emission from the *in situ* Er-doped GaN when excited by 404 nm (violet) light. In Fig. 5, the broadened PL peaks in the "blue-pumped" PL spectrum of the *in-situ* Er-doped sample do not correspond to the B-labeled PL peaks associated with the "blue" Er^{3+} site observed in the Er-implanted MOCVD-grown sample, but the PL of the Er-implanted HVPE-grown sample includes both the B- and A-labeled PL peaks. The "red-pumped" PL spectra in Fig. 6 show that while the 633 nm light excites the R (red)-labeled Er^{3+} emission as well as the B-, A-, N-, and O-labeled bands in the Er-implanted MOCVD GaN sample (Fig. 6b), only the B-labeled PL peaks are observable in the PL of the Er-implanted HVPE-grown sample (Fig. 6a), and no ~1540 nm emission is excited from the *in situ* Er-doped GaN.

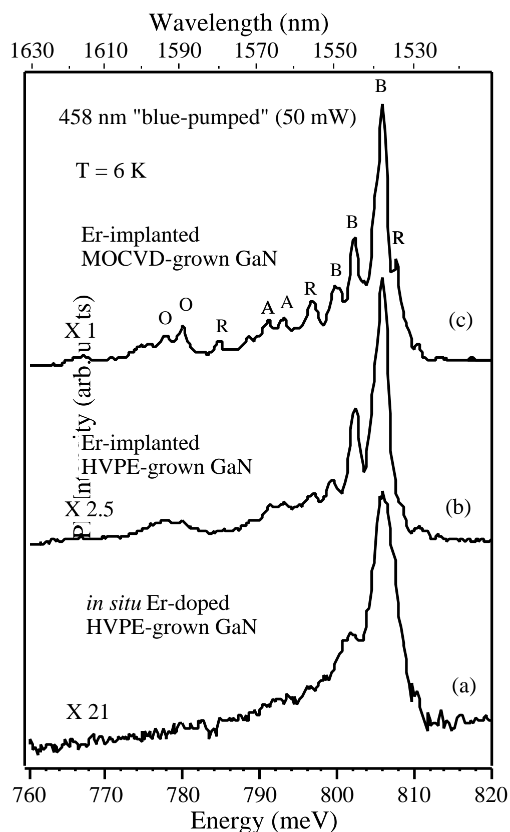

Fig. 5. The "blue-pumped" PL spectra as excited by blue light (458 nm).

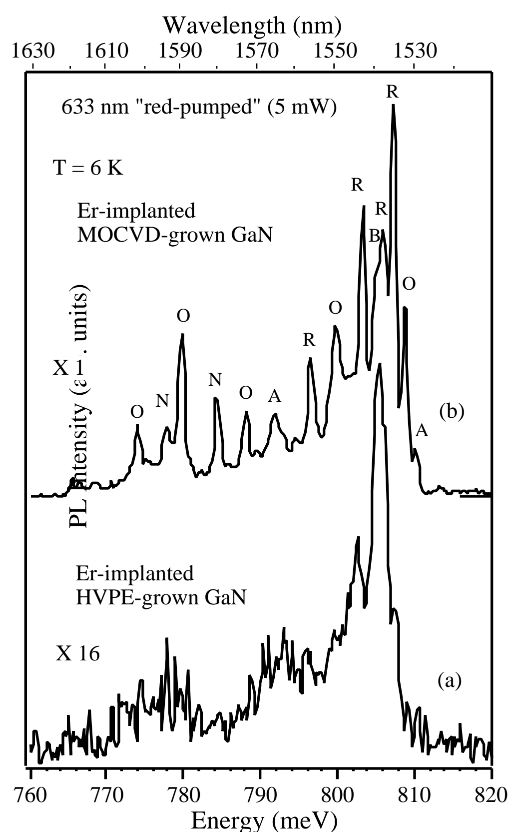

Fig. 6. The "red-pumped" PL spectra as excited by red light (633 nm).

The "4*f*-pumped" PL spectra in Fig. 7 were excited by 809 nm light that corresponds to direct Er^{3+} 4*f*-band absorption. Significantly, the "4*f*-pumped" PL spectrum of the Er-implanted HVPE-grown GaN (Fig. 7b) shows sharply-structured PL peaks that are nearly identical in peak energy and relative intensities to those of the Er-implanted MOCVD-grown GaN PL spectrum of Fig. 7c. This indicates that most of the Er atoms in the Er-implanted HVPE-grown GaN occupy a

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single type of high-concentration, isolated Er^{3+} center, that can only be excited by direct 4*f*-band absorption, and that this is the same high-concentration Er^{3+} center previously observed by direct 4*f*-band pumping in Er-implanted MOCVD-grown GaN [3,4]. In contrast, 4*f* pumping of the Er^{3+} dopants in the *in-situ* Er-doped GaN excites a broad 1540 nm PL spectrum (Fig. 7a) that is identical to the "green-pumped" PL spectrum (Fig. 1a) and the "blue-pumped" PL spectrum (Fig. 5a) for this sample, clearly demonstrating the absence in the *in-situ*-doped material of the multiple, selectively excited, discrete Er^{3+} sites or centers that are observed in the Er-implanted GaN. The broad 4*f*-pumped Er^{3+} PL spectrum confirms our earlier suggestion that the Er dopants in the *in-situ*-doped sample occupy sites located in disordered regions of the material and therefore experience site-to-site variations in the crystal field.

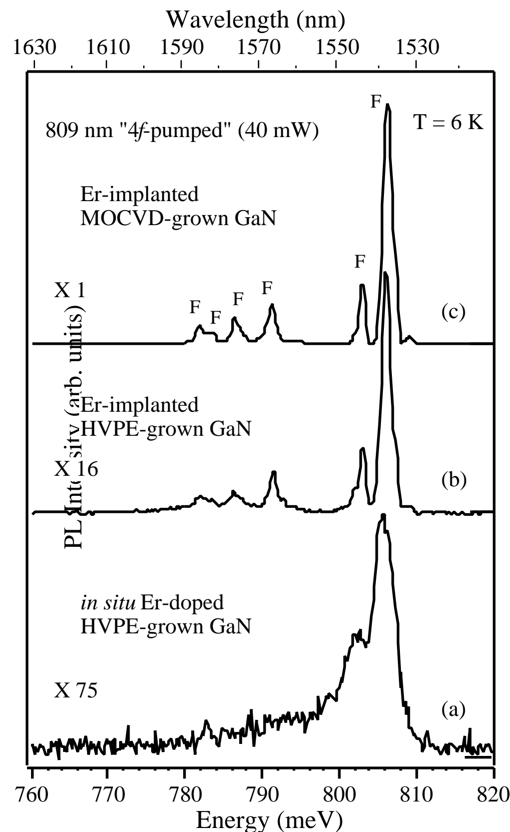

Fig. 7. The “4*f*-pumped” PL spectra as excited by 809 nm light.

CONCLUSIONS

Site-selective PLE and PL spectroscopy have been carried out at 6K on the 1540 nm $^4I_{13/2}$ $^4I_{15/2}$ emission of Er^{3+} in *in situ* Er-doped and Er-implanted GaN grown by HVPE. The PLE and PL spectra of these two different Er-doped HVPE-grown GaN films are compared in this study with Er-implanted GaN grown by MOCVD to see if the multiple, selectively excited, discrete Er^{3+} sites or centers observed in our previous studies of Er-implanted GaN are present in Er-doped GaN synthesized by other growth, doping and annealing procedures.

The PLE and PL spectroscopy of this study reveal that four of the seven different Er^{3+} sites observed in Er-implanted MOCVD-grown GaN annealed at 900 °C under a flow of N_2 are present in Er-implanted HVPE-grown GaN annealed at 800 °C in an NH_3/H_2 atmosphere. In contrast, the *in situ* Er-doped HVPE-grown GaN exhibits a single, broad ~1540 nm Er^{3+} PL spectrum whose lineshape is independent of excitation wavelength. This broad Er^{3+} PL spectrum, which is reminiscent of emission from an Er-doped glass, prompts the suggestion that the Er dopants in the *in-situ*-doped sample occupy sites located in disordered regions of the material characterized by site-to-site variations in the crystal field.

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