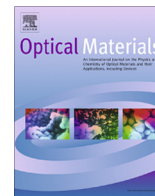




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Optical Materials

journal homepage: www.elsevier.com/locate/optmatProbing of local alloy disorder in InGaN using Er³⁺ ionsM. Stachowicz^{a,*}, A. Kozanecki^a, J.Y. Lin^b, H.X. Jiang^b, J. Zavada^c^a Institute of Physics, Polish Academy of Science, Al. Lotnikow 32/46, 02-668 Warszawa, Poland^b Department of Electrical and Computer Engineering, Texas Tech University, Lubbock, TX 79409, USA^c Department of Electrical and Computer Engineering, Polytechnic Institute of New York University, Brooklyn, NY 11201, USA

ARTICLE INFO

Article history:
Available online xxx

Keywords:
Rare earth
Luminescence
Energy levels
Lattice disorder

ABSTRACT

We report on studies to probe the local lattice disorder in InGaN:Er epilayers using the 1.54 μm emission of Er³⁺ ions. The InGaN layers were doped during MOCVD growth with Er to a concentration of about 2.3%. Site selective optical spectroscopy and excitation photoluminescence spectroscopy were used to show that in InGaN:Er two classes of the emitting Er centers can be distinguished: (i) one leading to emission of Er³⁺ which is nearly the same as in GaN:Er, except nonuniform broadening and (ii) another that yields new emission features not having its counterpart in GaN:Er. The latter emission is interpreted as originating from Er-complexes involving one or more In atoms in the second coordination sphere. The observed fluorescence line broadening and wavelength shifts in the emission wavelength indicate the extent of the disorder in the metallic sublattice.

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1. Introduction

Erbium doped semiconductors exhibit sharp intra-4f-shell luminescence that in wide-band gap materials such as GaN, persists to room temperature [1]. This has naturally led to the increased interest in studies of optical properties of Er in these materials. The 4f-shell of trivalent Er³⁺ and, in general of all other RE³⁺, is mainly insensitive to the host material, since wavefunctions of the 4f-electrons are highly confined in space and are very well screened by the outer closed 5s² and 5p⁶ shells. Crystal field theory predicts that splitting of the multiplets of RE impurities is determined by the intensity and symmetry of the crystal field acting upon them [2]. As a result, the local arrangements of atoms in the nearest neighborhood of the RE ion has the direct influence on the emission spectrum. Identification of the local structure of different RE-emitting centers is important for understanding their emitting properties and it may bring valuable information for technology of these materials for evaluation which of them are promising for efficient luminescence in optical devices.

In the case of III–V compounds no additional charge is introduced with the isoelectronic substitution of a group III metal ion with a RE³⁺ ion. Nevertheless, introduction of an atom with larger ionic radius may also lead to alteration of Stark splittings. This is due to modifications of local electric fields being a consequence of distortions and changes of the distances between host atoms

[3]. As a result, rare earth atoms can potentially be used also for probing of the local alloy disorder. A well defined position of a RE impurity is the necessary condition for using RE ions as probes of structural disorder, in particular, its substitutional location is highly desired. This condition is fulfilled for Yb in InP-based solid solutions, where Yb substitutes for In, as was proven by Kozanecki and Groetzchel [4] using Rutherford backscattering and channeling spectrometry. It was shown that owing to substitutional location photoluminescence (PL) of Yb³⁺ ions can be used to assess the alloy disorder in InPAs and GaInP [5].

Erbium in InGaN alloys seems to be a very good candidate for probing local atomic environment, as substitutional location of Er ions in GaN has been proven by channeling of He⁺ ions [6]. Site-selective optical spectroscopy measurements performed on MOCVD grown GaN heavily doped with Er during growth, confirmed that the emission near 1.54 μm comes almost exclusively from a single center of C_{3v} symmetry [7]. The existence of one dominant center in GaN:Er has recently been confirmed by Sedhein et al. [8]. This center in a natural way has been assigned to Er at substitutional position. The existence of a single emitting center due to substitutional position of Er makes studies of structural disorder in group III metal nitrides, such as InGaN or AlGaIn possible. We expect that observation of a single GaN-like Er-center (Er–4 N–12 Ga) will be possible for relatively low In contents. It also seems that another class of Er-complexes containing one or more In atoms substituting Ga atoms in the next-near-neighbor (NNN) positions to Er can be identified. The presence of two classes of centers should manifest themselves in the PL as an inhomogeneously broadened GaN-like

* Corresponding author. Tel.: +48 228436601.

E-mail address: stachow@ifpan.edu.pl (M. Stachowicz).

Er emission and a broad PL spectrum due to a relatively complex atomic disorder in the second coordination sphere around Er ions. To verify this idea layers of GaN and InGaN with 5% and 7% contents of In grown by MOCVD and doped with Er during growth were studied using photoluminescence (PL), the high resolution Fourier Transform Infrared PL (FTIR PL), and PL excitation (PLE).

Some preliminary results of the PL properties of Er^{3+} ions in InGaN (7% In) MOCVD grown layers implanted with Er were published by Correia et al. [9]. The authors showed that the emission of Er near $1.54 \mu\text{m}$ coming from InGaN layer appears after annealing at 400°C . This emission was shifted to slightly shorter wavelengths in comparison with the PL of Er in GaN, however, the PL lines were as sharp as for Er in GaN. This result is a little surprising, as nonuniform broadening due to alloy disorder should be expected. On the other hand it may suggest either the formation of GaN phase or another phase involving Er ions in well defined lattice positions.

In this paper we show that in Er-doped InGaN epilayers at least two classes of Er centers can be distinguished. One of which gives rise to the emission typical of Er in GaN, the other yields emission that indicates disorder in the material.

2. Experimental details

Erbium doped InGaN layers were grown by MOCVD technique on a GaN buffer layer deposited on sapphire. Details of the growth procedure were described in paper by Ugolini et al. [10]. The InGaN layers of $0.2 \mu\text{m}$ thick were grown on top of a GaN buffer and were doped with Er during growth. The concentration of Er was approximately 2.3%. The PL was excited with a 333 nm wavelength of an Ar^+ laser. The site selective and PL excitation (PLE) measurements were performed using a tunable Ti:sapphire laser pumped with an argon 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 and for some PL measurements a standard setup with a monochromator was used.

3. Results and discussion

In Fig. 1 the high resolution FTIR PL spectra taken at 6 K of GaN:Er, $\text{In}_{0.05}\text{Ga}_{0.95}\text{N:Er}$ and $\text{In}_{0.09}\text{Ga}_{0.91}\text{N:Er}$ epilayers excited with the 333 nm UV line are presented. The PL spectrum of GaN:Er

contains a number of sharp emission lines which, as mentioned above, are due to one emitting center [7]. The spectra of InGaN:Er are, as expected, much broader, particularly for a 9% In contents, reflecting disorder existing in the host caused by alloy mixing in metallic sublattice and by fluctuations in the compositions [11]. The full width at half maximum (FWHM) of the most intense peak of Er in GaN is 0.7 cm^{-1} , only slightly above the 0.5 cm^{-1} resolution of the FTIR spectrometer, while the FWHM of the most intense Er^{3+} peaks in InGaN are 20.8 cm^{-1} and 28.3 cm^{-1} in the samples with 5% and 9% of In, respectively. The PL spectrum of Er in $\text{In}_{0.09}\text{Ga}_{0.91}\text{N}$ reveals two distinct peaks at 6496.11 cm^{-1} and 6506.48 cm^{-1} . In the PL spectrum of Er in $\text{In}_{0.05}\text{Ga}_{0.95}\text{N}$ we can observe only one dominant peak at 6497.45 cm^{-1} .

In Fig. 2 the PL spectra excited resonantly to the $^4\text{I}_{9/2}$ state are presented. It can be noticed that the PL spectra of Er in both $\text{In}_{0.09}\text{Ga}_{0.91}\text{N:Er}$ and $\text{In}_{0.05}\text{Ga}_{0.95}\text{N:Er}$ are shifted slightly towards lower energies with respect to PL of GaN:Er. The main peak of the Er^{3+} PL in $\text{In}_{0.09}\text{Ga}_{0.91}\text{N}$ for the same excitation wavelength as for Er^{3+} in GaN (809.4 nm) is shifted by nearly 9 cm^{-1} , whereas for $\text{In}_{0.05}\text{Ga}_{0.95}\text{N:Er}$ it is about 3.5 cm^{-1} only. The line widths and the spectral positions of the Er^{3+} PL lines in GaN do not change in comparison with those observed at 333 nm excitation, however, some redistribution of the intensities between PL lines takes place. The PL spectra for both InGaN compositions are, as expected, narrower for resonant excitation than for 333 nm pumping. Similarities between the PL of Er^{3+} in GaN and InGaN with a 5% of In can be noticed (Fig. 2). The main difference is broadening in the case of $\text{In}_{0.05}\text{Ga}_{0.95}\text{N:Er}$ and broadening is particularly large for $\text{In}_{0.09}\text{Ga}_{0.91}\text{N:Er}$.

To determine whether the observed PL spectra of InGaN:Er epilayers are due to a single Er-center perturbed by alloy disorder or to a few different centers, the PLE spectra, excited from the $^4\text{I}_{15/2}$ ground state to the $^4\text{I}_{9/2}$ state, were measured at 6 K. The PL intensity was monitored at the main PL peaks at 6504.8 cm^{-1} for Er in GaN, 6496.1 cm^{-1} and 6497.5 cm^{-1} for Er in InGaN with 9% and 5% of indium contents, respectively. As shown in Fig. 3, the PLE spectra for both InGaN compositions and GaN differ remarkably. The spectrum for GaN:Er consists of several sharp lines with the dominant line at 809.5 nm . The spectra for InGaN:Er are much broader and on the short wavelength side, a broad excitation band not found in GaN:Er is observed. The higher is the concentration of In the larger is broadening of the absorption lines. The maximum intensity peaks in the spectra of Er^{3+} in InGaN:Er layers are situated at the same energy of $12355 \pm 1 \text{ cm}^{-1}$. We notice that the concentration of Er dopant

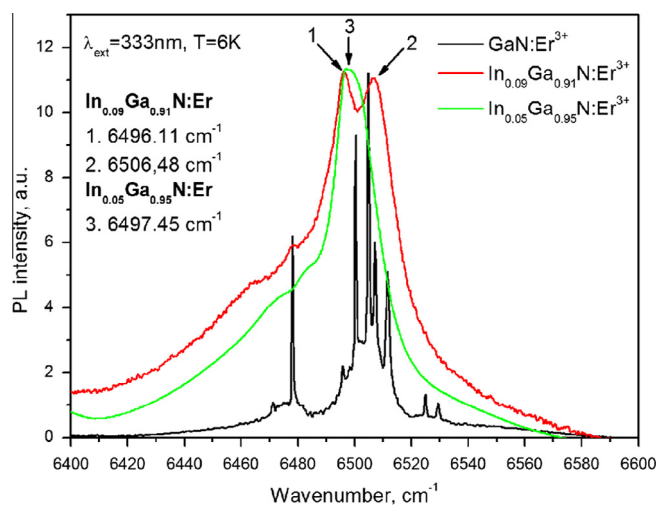


Fig. 1. PL spectra of Er^{3+} in GaN and InGaN alloys excited with $\lambda_{\text{exc}} = 333 \text{ nm}$.

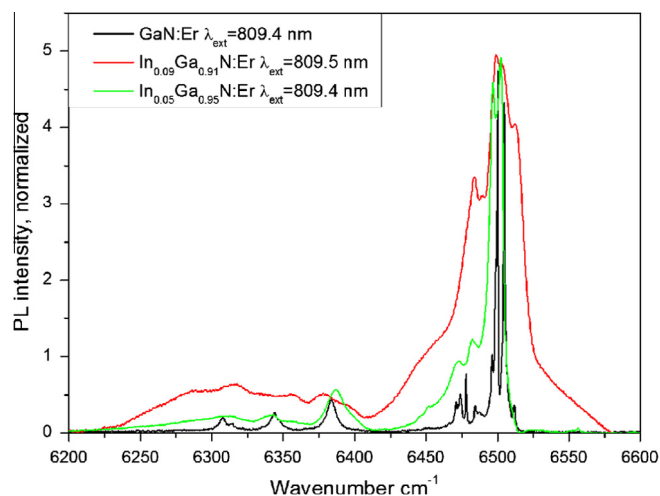


Fig. 2. PL spectra of Er^{3+} in GaN and InGaN alloys at 6 K excited resonantly to $^4\text{I}_{9/2}$ state.

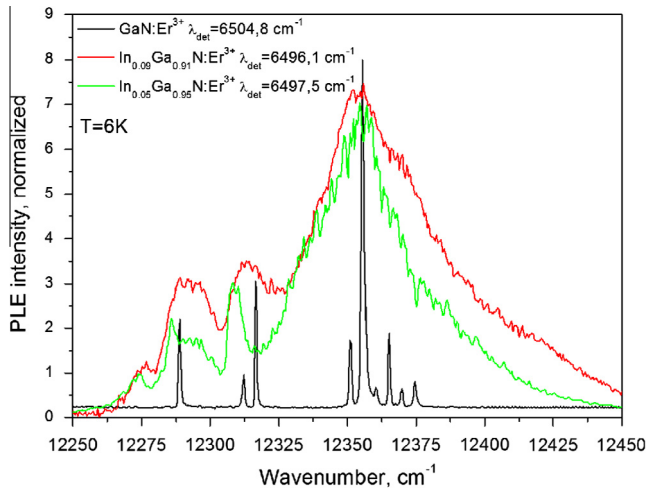


Fig. 3. PLE spectra of Er^{3+} in GaN and InGaN alloys at 6 K.

though high, is still much below the value of 5% which has been established as optimal [14], above which the PL intensity tends to decrease.

Site selective PL spectra of Er^{3+} , measured at excitation wavelengths on the short wavelength side (806.5–809.0 nm) of the PLE spectra, are presented in Fig. 4a and b for $\text{In}_{0.09}\text{Ga}_{0.91}\text{N}$ and $\text{In}_{0.05}\text{Ga}_{0.95}\text{N}$, respectively. No sharp transitions that could be

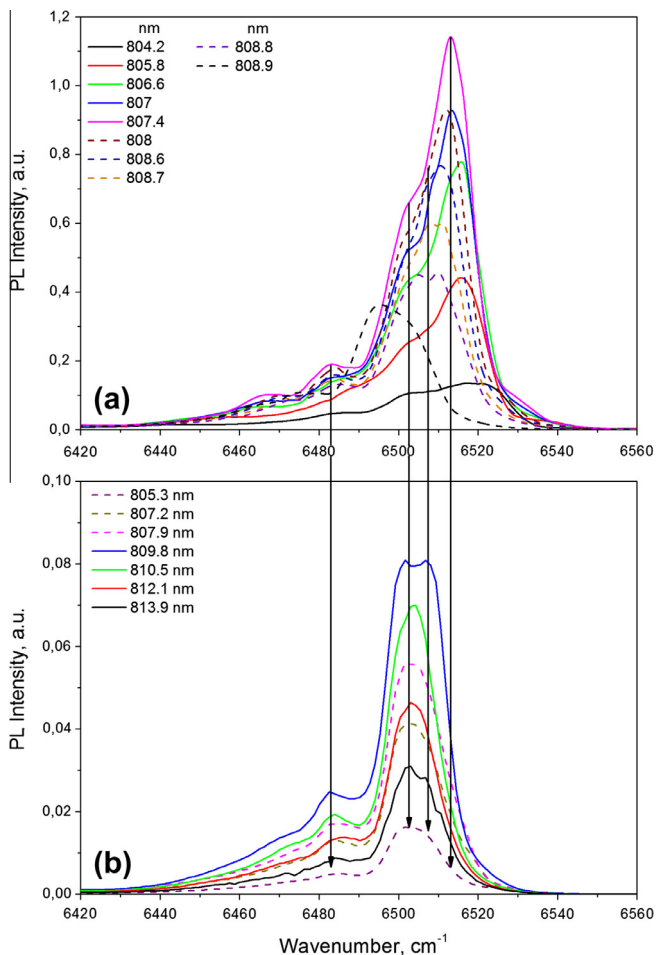


Fig. 4. Site selective spectra of: (a) Er in $\text{In}_{0.09}\text{Ga}_{0.91}\text{N}$ at $T = 6$ K (b) Er in $\text{In}_{0.05}\text{Ga}_{0.95}\text{N}$ at $T = 6$ K.

ascribed to the emission of Er in GaN phase are observed, so we believe that InGaN layers do not contain precipitates of GaN:Er.

As it is seen in Fig. 4b, in the case of $\text{In}_{0.05}\text{Ga}_{0.95}\text{N}:\text{Er}$ there is no shift of the spectra along with changes of the excitation wavelength and, moreover, fluorescence line narrowing is not observed. The shape of the spectra does not, in principle, depend on excitation wavelength. It suggests that an admixture of a 5% of In into GaN:Er does not create a measurable concentration of any new class of Er-centers which could be detected in luminescence. The only measurable contribution of In admixture into PL is inhomogeneous broadening of the PL due to alloying of GaN with indium. The character of the spectra in Fig. 4b suggests that inhomogeneous broadening of the Er energy levels does not lead to their significant overlap.

The PL spectra of InGaN 9% behave in a more complex way than those for a 5% InGaN. In particular, the PL maximum in a 9% InGaN moves to longer wavelengths following changes of the excitation wavelength. It can also be seen that spectral position of a shoulder at 6505.7 nm remains independent of excitation wavelength and, moreover, its double peak structure of InGaN 5%, clearly resolved for 809.5 nm excitation, is also repeated for excitation wavelengths from 807.7 to 808.8 nm.

The observed character of the site selective spectra in this InGaN layer can be interpreted as reflecting fluorescence line narrowing due to selective excitation of small subsets of Er-centers within the whole family of the emitting centers in Er doped InGaN compounds. Such fluorescence narrowing was observed in many RE doped materials including Er in glasses [12] and silica [13]. However, nonuniform broadening in glasses is at least a factor of 4–5 greater than for InGaN found here ($\sim 15 \text{ cm}^{-1}$ for 9% of In contents).

Site selective spectra of a 9% InGaN are shifted to slightly higher energies in comparison to the sample with 5% of In for the same excitation wavelengths. This is due to much larger broadening of the energy levels in the 9% InGaN. Nevertheless, it seems that in both samples we can distinguish the PL at 6507 cm^{-1} coming from the same type of Er-center. The comparison of the spectra with that for GaN allows to conclude in both InGaN epilayers a very similar center as in GaN exists, most probably associated with the substitutional Er^{3+} ion surrounded with 4 N atoms. The presence of In in the second coordination sphere acts as perturbation contributing to broadening. Very similar behavior of the PL as a function of Ga contents was observed in GaN:P:Yb – for low contents of Ga, only inhomogeneous broadening of the Yb-related PL lines without spectral shift was observed, whereas for high Ga contents the PL spectrum of Yb^{3+} transformed itself into a single broad band [5].

At this point we like to stress that the PL spectra only weakly depend on the position of the excitation beam on the sample, which points to a good uniformity of the $\text{InGaN}:\text{Er}^{3+}$ layers. The high crystalline quality of $\text{InGaN}:\text{Er}$ was confirmed by the results of Sedhein et al. [8]. Their X-ray diffraction measurements of $\text{In}_{0.05}\text{Ga}_{0.95}\text{N}:\text{Er}$ showed that the crystalline quality of InGaN sample is as good as those of Er doped GaN and the FWHM values of 002 diffraction peak is 462 arcsec. The AMF measurements of surface roughness revealed the RMS at the level of 4 nm. The Er concentration was confirmed by secondary ion mass spectroscopy measurements.

The results of our work can be summarized in energy level schemes proposed in Fig. 5. The schemes reflect two cases: (i) when inhomogeneous broadening of the energy levels is too small to overlap significantly (5% InGaN) and, (ii) when partial overlap of the levels (in a 9% of InGaN) takes place. Because of the larger broadening of the energy levels in InGaN with 9% of In the PL can be excited selectively with shorter wavelength than in InGaN 5%, which results in emission with slightly higher energy.

The results presented in this work suggest that two classes of the spectra can be distinguished in $\text{InGaN}:\text{Er}$. One is similar to that

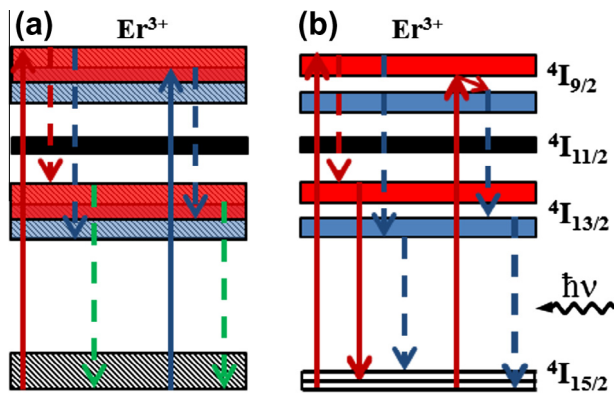


Fig. 5. Schematic representation of excitation and PL of Er^{3+} in: (a) $\text{In}_{0.09}\text{Ga}_{0.91}\text{N}$ and (b) $\text{In}_{0.05}\text{Ga}_{0.95}\text{N}$.

of GaN:Er, however, inhomogeneously broadened due to the structural disorder. The second contributing substantially to PL in 9% In-GaN does not have a counterpart in the emission from GaN:Er and $\text{In}_{0.05}\text{Ga}_{0.95}\text{N:Er}$. In the InGaN host, an Er ion ideally has 4 N atoms in the nearest positions and a mixed configuration of metal atoms in the second nearest positions. Statistically, assuming the entirely random distribution of metallic ions in the mixed sublattice of In-GaN with low In contents, the dominant configuration around Er ions should involve no In, or one In atom in the NNN positions. Of course, complexes with 2 or more In atoms in NNN positions are possible, particularly for a 9% In contents. In the latter case it is difficult to presume that such centers could be resolved spectrally with respect to different nonequivalent positions of two or more In atoms. Therefore, such centers will contribute mostly to nonuniform broadening of the PL and PLE lines.

The existence of a GaN-like Er center (no In atoms in the NNN positions) seems to be proven by the data presented in Fig. 4. The centers giving rise to the emissions shown in Fig. 4b can be ascribed to complexes containing at least one In atom in the NNN positions. This interpretation is valid for random statistics of In atoms, as well as for non-random local fluctuations of the composition, often observed in InGaN [11]. A consequence of alloy disorder and compositional fluctuations is the large width of the PL lines and fluorescence line narrowing (Fig. 4a and b) of the Er emission at resonant excitation. Assuming a random distribution statistics of In and Ga atoms in the mixed sublattice, the probability $P(x_n)$ that Er is surrounded in NNN positions is given by the binomial distribution:

$$P(x_n) = \binom{12}{n} x^n |1 - x|^{(12-n)},$$

where x is the fraction of indium. For a 5% In contents the probability of finding no In atom in the NNN position is 0.54, and for $x = 9\%$ such a probability is 0.32. The probability of finding an environment with $n \geq 2$ In atoms in NNN positions is low in comparison with configurations with $n = 0$ and $n = 1$, so in the InGaN samples under study the GaN-like Er-4 N centers should be easily observed in both epilayers, as shown in this paper. Observation of fluorescence line narrowing in the spectra of a $\text{In}_{0.09}\text{Ga}_{0.91}\text{N:Er}$ is due to a large non-uniform broadening of the Er^{3+} energy levels resulting in their overlap (Fig. 4a).

4. Summary

In summary, we have shown that in MOCVD grown InGaN:Er two classes of the emitting Er centers are observed: (i) one leading to GaN:Er-like emission which is, however, nonuniformly broadened; and, (ii) another yielding new emission bands that do not have a counterpart in GaN:Er. The latter emission is interpreted as originating from Er-complex (or complexes) involving at least one In atoms in the second coordination sphere. This center is responsible for the observed fluorescence line narrowing and shifts in wavelength following changes in excitation wavelength. The observed fluorescence data indicate that the large width of the PL and PLE lines is due to alloy disorder or fluctuations of composition in the Er-doped layer.

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