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Spectroscopic characterization of Praseodymium doped Gallium Nitride powder prepared by a Na flux method

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ABSTRACT

The photoluminescence (PL) properties of Pr^{3+} doped GaN powders prepared by a Na flux method were investigated. Under above- and below-gap excitation, GaN:Pr powders exhibited intense red emission lines centered at ~650 nm corresponding to the intra-4f transition $^3P_0 \rightarrow {}^3F_2$ of Pr^{3+}. In addition, weak infrared PL bands were observed from lower excited states of Pr^{3+} at ~960, ~1300, and ~1500–1700 nm. A temperature dependent study of the red emission showed that the integrated PL intensity decreased by a factor of two under above-gap excitation for the temperature range 10–300 K. No significant thermal quenching of the red Pr^{3+} PL was observed under below-gap excitation. Time-resolved emission studies revealed that the decay transient of the red PL was characterized by a fast non-exponential decay followed by a slower decaying exponential component. The non-exponential decay can be attributed to cross-relaxation processes among Pr^{3+} ions, whereas the exponential component suggests the existence of isolated Pr^{3+} centers not affected by emission quenching through cross-relaxations.

1. Introduction

Over the last decade, light emission from rare-earth (RE) doped wide band gap III-nitride semiconductors has been intensively studied for applications in display technology, solid-state light sources, and optical communications [1–5]. Since the RE emission intensity is not significantly affected by thermal quenching in wide band-gap semiconductors, III-nitride alloys have proven to be promising host materials for RE doping [6]. Results have been reported on *in situ* doping and ion-implantation of RE ions into GaN, AlN, and AlGaN thin-films [1–4,7–9]. Among the III-nitrides, GaN is an excellent host because it has a direct band gap and it allows the incorporation of high RE concentrations [5]. Light emission in the UV, visible, and IR spectral region has been reported from several RE doped GaN systems prepared by different growth techniques [2–4,7–10].

Pr^{3+} doping of GaN has been of interest for photonic applications due to the strong red emission at ~650 nm and IR emission at ~1300 nm [11–13]. There are several reports regarding photoluminescence (PL), electroluminescence (EL), and cathodoluminescence (CL) in the red spectral region from Pr^{3+} doped GaN films grown by ion implantation, solid source MBE, and metal-organic chemical vapor deposition (MOCVD) [11–19]. Although considerable research has been done on RE doped GaN, questions concerning the RE incorporation, excitation mechanisms, and local crystal-field symmetry still remain. Wahl et al. studied the lattice location of Pr^{3+} implanted GaN using emission channeling technique and reported that substitutional Ga sites are thermally stable lattice positions for Pr^{3+} ions in GaN [15]. Gruber et al. calculated the crystal-field splitting of Pr^{3+} energy levels in Pr implanted GaN films grown by MOCVD [16]. Effects of the oxygen incorporation and thermal annealing on the red PL intensity of Pr implanted GaN samples were investigated by Zavada et al. [13] and others [17,19].

Recently, RE doped GaN powders have been prepared for potential applications as phosphors in displays and solid-state lighting using different methods including flux techniques and combustion synthesis [20–25]. Wu et al. [21,22] reported green and red emissions from Er and Eu doped GaN powders, respectively. The visible PL and CL properties of Eu and Tb doped GaN nano-crystallites were investigated by Nyk et al. [25]. To our knowledge, there has been no report on the PL properties of Pr^{3+} doped GaN powder. In this work results of the emission properties of Pr^{3+} doped GaN powders prepared by a Na flux method are presented. Steady-state and time-resolved PL studies were performed as a function of excitation wavelength and temperature.

2. Experimental details

GaN crystallites and powders were prepared from a Na–Ga melt heated at temperatures of 600–800 °C and N_2 pressures of approximately 5 MPa. Pr metal (1.2 at.%) was added into the Na–Ga melt. After heating for 200 h, the sample was cooled down

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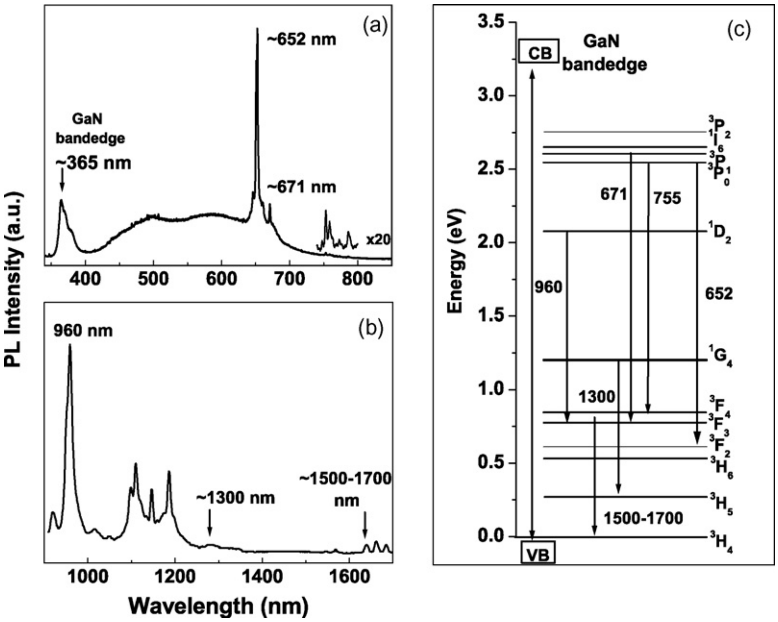

Fig. 1. Room temperature visible (a) and infrared (b) PL spectra from Pr doped GaN powder under above-gap UV excitation. (c) Schematic energy level diagram of the intra-4f levels of Pr^{3+} ions in GaN. The observed visible and near-IR emission lines of Pr^{3+} are indicated in the diagram.

to room temperature. The solidified Na–Ga melt was removed from the GaN crystals by adding ethanol first and then using a nitrohydrochloric acid solution to dissolve the remaining Na–Ga intermetallic compounds. More details of the sample preparation were described elsewhere [23]. Fragments of the Pr doped GaN crusts were powdered with an agate pestle and a mortar. The powder was pressed into pellets (~2–3 mm diameter) for the emission measurements.

PL characterization was performed using either a He–Cd laser (325 nm) or a UV argon laser (333.6–363.8 nm) for above-gap excitation. A diode-pumped solid-state (DPSS) laser operating at 473 nm was used for below-gap excitation. The visible PL was analyzed by a 0.5 m monochromator in conjunction with a photomultiplier tube. The IR PL was dispersed by a 1 m monochromator and detected with an InGaAs detector. The spectral resolution in visible PL studies was ~1 nm, whereas IR PL spectra were recorded with lower resolution (~10 nm) due to weaker signal intensities. For PL decay time measurements, the third harmonic output of a pulsed Nd:YAG laser (355 nm) was used for above-gap excitation. A Nd:YAG pumped optical parametric oscillator (OPO) system (10 ns pulses, 10 Hz) was employed for resonant pumping at ~473 nm. The decay signals were recorded by averaging the detector signal on a digital oscilloscope. Temperature dependent PL studies (10–300 K) were carried out using a two-stage closed-cycle helium refrigerator.

3. Results and discussion

Fig. 1(a) and (b) shows the overview PL spectra of GaN:Pr powder in the visible and near-IR spectral regions at room temperature. Under above-gap excitation the sample exhibited GaN bandedge emission at ~365 nm, a defect-related background emission centered at ~550 nm, and strong red emission lines centered at ~650 nm which corresponds to the $^3P_0 \rightarrow {}^3F_2$ transition of Pr^{3+} ions (Fig. 1(a)). The full width at half maximum (FWHM) of the ~650 nm PL line was ~3 nm at 300 K. A few weaker emission lines were observed at ~671 nm ($^3P_1 \rightarrow {}^3F_3$) and ~750–800 nm ($^3P_0 \rightarrow {}^3F_4$,

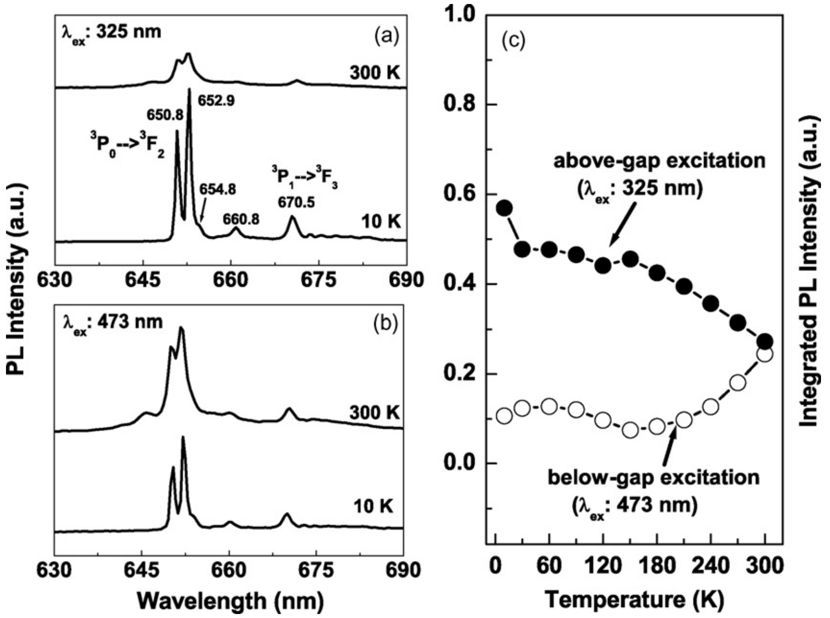

Fig. 2. High-resolution PL spectra of the red emission line of $^3P_0 \rightarrow {}^3F_2$ at 10 and 300 K from GaN:Pr powder under (a) above-gap excitation and (b) below-gap excitation. (c) Temperature dependence of the integrated Pr^{3+} PL intensities for above-gap and below-gap excitations.

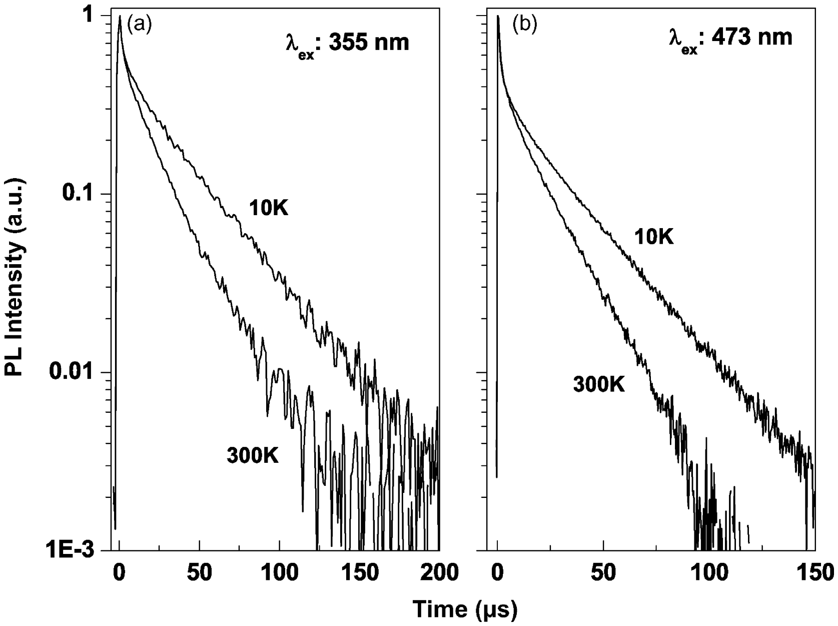

Fig. 3. Decay transients of the red PL ($^3P_0 \rightarrow {}^3F_2$) from GaN:Pr following pulsed excitation for (a) above-gap pumping and (b) below-gap pumping. The emission was monitored at ~652 nm.

$^1D_2 \rightarrow {}^3H_6$) [13,14]. Besides the visible PL, near-IR emission lines from Pr^{3+} were observed at ~0.91–1.0, ~1.3, and ~1.5–1.7 μm corresponding to the $^1D_2 \rightarrow {}^3F_3$, $^1G_4 \rightarrow {}^3H_5$, and $^3F_3$, $^3F_4 \rightarrow {}^3H_4$ transitions (Fig. 1(b)). Additional emission lines were noted at 1108, 1145, and 1185 nm, but the origin of these lines has not yet been identified [11–13]. A schematic energy level diagram of Pr^{3+} depicting all identified PL lines is shown in Fig. 1(c) along with the GaN energy gap. The visible and IR PL spectra of Pr doped GaN powder agree well with previous reports on Pr implanted GaN and MBE grown Pr doped GaN thin-films [11–13]. For the remainder of this paper, attention is focused on the red emission properties of Pr doped GaN powder.

The high-resolution emission spectra of GaN:Pr powder at 10 and 300 K under above-gap (325 nm) and below-gap (473 nm) excitations are shown in Fig. 2. No significant spectral differences were observed for both excitation wavelengths, which suggest that similar Pr^{3+} centers are excited. At low-temperature, several PL lines were resolved with peaks at 650.8, 652.9, 654.8, 658.2, 660.8, and 670.5 nm. Many authors have discussed that RE ions predominantly enter the substitutional Ga^{3+} lattice sites in GaN with trigonal C_{3v} symmetry [14–16,18]. Assuming that Pr^{3+} ions are located in C_{3v} symmetry for the investigated GaN:Pr powder, the dominant lines at 650.8 and 652.9 nm (including a weak shoulder at 654.8 nm) are assigned to the expected crystal-field components of the $^3P_0 \rightarrow {}^3F_2$ transition. The weaker visible emission lines at longer wavelengths are most likely due to other $^3P_J \rightarrow {}^3F_J$ transitions of Pr^{3+} [14].

The temperature dependence of the integrated Pr^{3+} PL intensity of the dominant red emission lines at ~650 nm under above and below-gap excitations is shown in Fig. 2(c). The integrated PL intensity was reduced by a factor 2 between 10 and 300 K for above-gap pumping. Under below-gap excitation, no significant thermal quenching of the red PL intensity was observed for the same temperature range. The Pr^{3+} PL quenching under above-gap excitation is tentatively attributed to a slight reduction in excitation efficiency with increasing temperature [26].

The decay transients of the red PL ($^3P_0 \rightarrow {}^3F_2$) at 10 and 300 K for above- and below-gap excitation are shown in Fig. 3. The PL was monitored at 652 nm. In both cases, the observed decay transients had two distinguishable components, a fast non-exponential component and a slower decaying exponential component. The non-exponential decay component can be due to several processes including multiple RE^{3+} centers, energy transfer, and cross-relaxation processes [27,28]. Since no significant spectral differences were observed for different excitation wavelengths, the contribution of multiple Pr^{3+} centers to the non-exponential decay component is considered to be small. As discussed by Lozykowski et al. for Pr implanted GaN films, the dominant contribution to the non-exponential decay is due to cross-relaxation between Pr^{3+} ions [14]. On the other hand, the exponential decay component suggests the existence of isolated Pr^{3+} centers not affected by emission quenching through cross-relaxation processes [14,29]. At low temperature, the slower decay component was determined to be ~38 μs for above-gap pumping and ~30 μs for below-gap excitation. A similar radiative decay rate of 38.9 μs was reported for Pr implanted GaN at 12 K under UV excitation [14]. An extrapolation of the exponential component to $t = 0$ shows that the ratio of the slow decay component to the total decay transient is ~35% for above-gap excitation. This value is significantly larger than the ~12% reported for Pr implanted GaN under UV excitation. This observation suggests that for the investigated GaN:Pr powder, Pr^{3+} ions are less affected by emission quenching through cross-relaxation than reported for Pr implanted GaN films. At room temperature, the exponential decay component decreased slightly to values of ~26 μs and ~20 μs for above-and below-gap pumping, respectively. The slight temperature dependence of the exponential decay component can be explained by the onset of weak non-radiative decay through multi-phonon emission and/or energy transfer to defects [30]. Further studies on the red PL quenching mechanisms in GaN:Pr powders are still in progress.

4. Summary

The PL emission properties of Pr doped GaN powder prepared by a Na flux method were investigated. Under above- and below-gap pumping, the sample exhibited bright red emission at 652 nm, which is of interest for applications in displays and solid-state lighting. The observation of near-IR emission lines at 0.96, 1.3 and ~1.5–1.7 μm indicates that GaN:Pr powder is also of interest for IR light source development and optical communications. Under UV excitation the integrated PL intensity at ~652 nm ($^3P_0 \rightarrow {}^3F_2$)

decreased by a factor of two between 10 and 300 K, whereas no significant PL quenching was observed for resonant intra-4f excitation using below-gap pumping. Emission decay time studies revealed that the majority of Pr^{3+} ions are impacted by cross-relaxation processes quenching the red emission from the $^3P_0 \rightarrow {}^3F_2$ transition. At the same time, the observation of a slower and exponential decay component suggests the existence of isolated Pr^{3+} centers not influenced by cross-relaxation emission quenching. Further time-resolved emission studies and decay time modeling are planned in the future to gain a better understanding of non-radiative quenching processes in Pr doped GaN powders.

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