Photoluminescence and Cathodoluminescence of GaN doped with Pr

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ABSTRACT

In this paper we have reported the observation of visible photoluminescence (PL) and cathodoluminescence (CL) of Pr implanted in GaN. The implanted samples were given isochronal thermal annealing treatments at a temperature of 1100^0 C in NH_3, N_2, Ar_2, and in forming gas $N_2 + H_2$, at atmospheric pressure to recover implantation damages and activate the rare earth ions. The sharp characteristic emission lines corresponding to Pr^{3+} intra-$4f^n$ -shell transitions are resolved in the spectral range from 350 nm to 1150 nm, and observed over the temperature range of 12 K-335 K. The PL and CL decay kinetics measurement was performed for $^3P_1$, $^3P_0$ and $^1D_2$ levels.

INTRODUCTION

Rare earth (RE) doped semiconductors have been of considerable interest for possible applications in light emitting devices and for their unique optical properties. The rare earth luminescence depends very little on the nature of the host and the ambient temperature. Recently CL and PL emission has been obtained over the visible and near infrared spectrum range from GaN grown on sapphire by MOCVD, and doped by implantation with Sm, Dy, Ho, Er, and Tm [1,2a,b]. The visible PL and EL emission have been obtained from Pr and Eu doped GaN grown by MBE on sapphire and Si substrates [3a, b].

EXPERIMENTAL DETAILS

The GaN material used for this investigation was grown by MOCVD on the basal plane of 2 inch diameter sapphire substrates. The thicknesses of the epilayer was 1.8 µm, and electron concentrations 5×10^{16} cm^{-3}. The implanting ion beam was inclined at 7^0 to the normal of the GaN epilayer to prevent channeling. The GaN was high quality undoped n-type epilayer implanted at room temperature with praseodymium. Pr was implanted at three energies at doses chosen to give an approximation of a square concentration implant profile in the GaN epilayer (the projected range and peak concentration were ~ 40 nm, and ~ 3.1×10^{19} cm^{-3} respectively). Samples were given

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postimplant isochronal thermal annealing treatments (duration 0.5 h and 1 h) at temperature 1100^0C in NH_3, N_2, Ar_2, and in forming gas (N_2+H_2). The emission spectra presented are obtained from samples annealed at 1100^0 C, which seems to be the optimal annealing temperature for RE ions incorporated as the luminescent center.
The photoluminescence spectra and kinetics measurements were performed using a He-Cd (325 nm) and N_2 (337 nm) lasers. The PL kinetics were measured using a double grating monochromator DIGIKROM CM112 assembled with Hamamatsu R928 (or R616) photomultipliers and a photon counting system with a turbo-multichannel scaler (Turbo-MCS, EG&G). The CL was excited by an electron beam incident upon the sample at a 45^0 angel from an electron gun (Electron gun system EK-2035-R (500V and 20 kV) which was in a common vacuum (of $\sim 5\times10^{-7}$ torr) with the cryostat.

ENERGY LEVELS, AND EXCITATION PROCESSES

The very important question is where the trivalent rare earth ions are incorporated in GaN: at substitutional sites on the metal sublattice and/or interstitial sites. In a hexagonal GaN crystal the Ga atoms occupy sites of symmetry C_{3v} (similar to Zn atoms in ZnS wurtzite phase) and two distinct high-symmetry interstitial positions also with C_{3v} symmetry[4a,b]. Recently, using the emission channeling (EC) technique, the lattice site occupations of RE elements in GaN were determined as a relaxed substitutional Ga-sites with an average relaxation of about 0.025 nm [5]. The rare earth ions can also aggregate especially at high concentration, as well as create complex centers in the presence of an anther ion e.g. oxygen . In this paper we studied the PL and CL and kinetics of GaN implanted with Pr. The Pr^{3+} free ion possesses $4f^2$ configuration which gives rise to a $^3H_4$ ground state and $^3H_{5,6}$, $^3F_{2,3,4}$, $^1G_4$, $^1D_2$, $^3P_{0,1}$, $^1I_6$, $^3P_2$, and $^1S_0$ excited states. If the crystal field symmetry at the Pr^{3+} site is known, then the number and symmetry of crystal field levels and the selection rules for transitions between these levels can be calculated. In C_{3v} crystal symmetry the states with $J = 0, 1, 2, 3, 4, 5, 6$, will split into 1(0), 1(1), 1(2), 3(2), 3(3), 3(4), 5(4), single(doubly) degenerate crystal field LSJ levels, respectively. The rare earth ions located at a specific crystal site are associated with characteristic optical transitions subject to the selection rules that are governed by the crystal symmetry of the site. It is generally accepted that rare earth impurities in III-V semiconductors create isoelectronic traps [6]. The outer electron configurations of RE^{3+} ions are the same $(5s^2 5p^6)$. If the RE^{3+} ions replace the element from column III(Ga^{3+}) in GaN semiconductors that are isovalent concerning outer electrons of RE^{3+} ions, we believed that they create isoelectronic traps in III-nitrides (REI-trap). That conclusion is supported by the fact that the atomic covalent radii (ionic RE^{3+}) for all rare earths are bigger than atomic radii of Ga that they are replacing. Pauling's electronegativity of RE elements (1.1-1.25) is smaller than Ga (1.81), for which it substitutes. We have evidence that the RE ion in III-V semiconductors can occupy different sites (not only substitutional). They can create more complex centers involving other impurities or native defects. The experimental data shows that RE ions introduce electron or hole traps in III-V semiconductors, and we do not have any evidence that RE ions act as a donor or acceptor. The nature of the RE isoelectronic trap (electron or hole trap) in III-nitrides must be determined. Knowledge about the microscopic structure of RE centers in III-nitrides is crucial for understanding the excitation processes of *4f-4f* transitions which in turn can determine the future of the RE dopants in optoelectronic applications.

The excitation processes of RE ions can be generally divided into two categories, direct and indirect excitation processes. The direct excitation process occurs in selective excitation of $4f^n$ electrons by photons (PL selective excitation) or in CL and EL by collision with hot electrons. Indirect excitation process occurs via transfer of energy to the $4f^n$ electron system from electron-hole pairs generated by photons with higher energy than the bandgap (PL excited above bandgap), injected in forward bias p-n junction, or generated by hot carriers in CL and EL. An excitation mechanism in CL and EL involves direct impact excitation of RE^{3+} ions by hot electrons, as well as an energy transfer from the generated electron-hole pairs or by impact excitation (or ionization) involving impurity states outside the $4f$ shell, with subsequent energy transfer to this shell. The most important excitation mechanism, from applications point of view, is the excitation of the RE ions by energy transfer process from electron-hole pairs generated in conduction and valence bands (by photons, hot electrons-CL) or injected in a forward bias p-n junction. There are three possible mechanisms of energy transfer. The first is the energy transfer process from excitons bound to structured isoelectronic centers to the core electrons. The second mechanism is the transfer of energy to the core electrons involving the structured isoelectronic trap occupied by electron (hole) and free holes (electrons) in the valence (conduction) band. The third mechanism is the transfer through an inelastic scattering process in which the energy of a free exciton near a RE structured trap is given to the localized core excited states. If the initial and final states are not resonant, the energy mismatch must be distributed in some way, e.g., by phonon emission or absorption.

LUMINESCENCE

In this paper, we present PL and CL spectra of Pr^{3+} in GaN in the spectral region of 350 to 1150nm. The luminescence of Pr^{3+} was excited indirectly, generating electron-hole pairs in GaN hosts by He-Cd, or N_2 lasers, and by electron beam excitation during CL measurement. Figure 1 shows two spectra CL (a) and PL (b) normalized to unity at peak (3) taken at 13 K and 330 K. The observed spectra shown in Fig.1, undoubtedly exhibit all the features of a trivalent rare earth ion.

Very weak luminescence was observed from $^3P_2$, $^1I_6$, $^3P_1$ levels (not
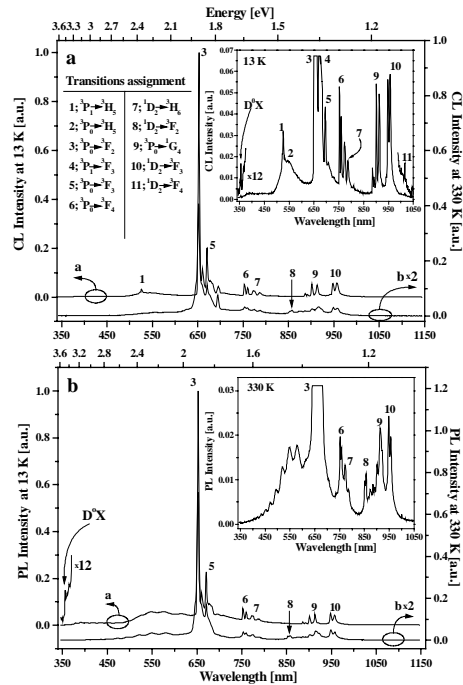

Fig.1 CL (a) and PL (b) spectra of GaN: Pr^{3+} recorded at 13 K and 330 K Inserts show magnified lower intensity emission lines of CL (a) and PL (b) spectra respectively. Numbers refer to transitions assignment from Fig. 1a.
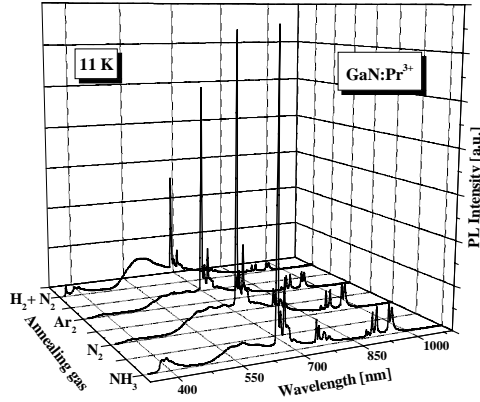
Fig.2 PL spectra of GaN: Pr^{3+} annealed at 1100^0 C during 1h in NH_3, N_2, Ar_2, and in forming gas

all marked in Fig.1), and strong luminescence from $^3P_0$, and $^1D_2$ levels. To show the weaker manifolds lines we enlarged the CL and PL spectra recorded at 13 K and 330 K as show in inset of Fig.1 a and b. A sharp CL emission line assigned to $^3P_1 \rightarrow ^3H_5$ transition (inset Fig.1 a) is only weakly seen on the short wavelength side of the interference modulated PL wide band (in spectral region ~ 400 - 600 nm) observed at 330 K in inset Fig.1 b. The nature of this wide band is not clear. The origin of it can be due to commonly observed "yellow band" overlapped partially with unresolved transition lines starting from $^3P_2$, $^1I_6$ $^3P_1$ $^3P_0$ levels. The assignments for the Pr^{3+} transitions in GaN have been made by comparison with data from other papers for the trivalent praseodymium ions in different crystals [7a,b].

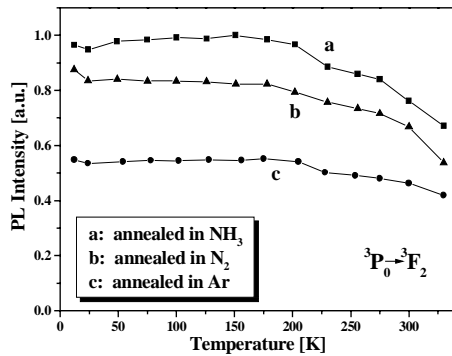Fig.3 The PL intensity of GaN: Pr^{3+} annealed at 1100^0 C during 1h in NH_3, N_2, Ar_2, monitored $^3 \rightarrow ^3$

Figure2 shows PL spectra of GaN: Pr annealed at 1100^0 C during 1h in NH_3, N_2, Ar_2, and in forming gas (N_2+H_2), at atmospheric pressure. The temperature dependence of intensity (area under curve) for dominant transition $^3P_0 \rightarrow ^3F_2$ plotted in Fig. 3 shows that the Pr^{3+} luminescence quenching is weak. The sample annealed during 1 h exhibits about two times stronger emission than the sample annealed during .5 h.

DECAY TIME MEASUREMENTS

The quenching of luminescence from rare earth ions doped semiconductors is very important for optoelectronic applications, and has been the subject of many investigations. That controls the quantum efficiencies and the luminescence lifetimes of rare earth ions. In our study we concentrate on measurements of lifetimes of the RE fluorescent levels as a function of temperature. The study of PL quenching of the singly doped (Pr^{3+}) GaN with temperature can provide information on interaction between like ions, ions with native defects and ions with unintentionally incorporated impurities. At low concentrations of praseodymium in GaN, the Pr^{3+} ions

form a disordered system with wide range of inter-ion separations. For a resonant process an excitation can be transferred from the excited donor D^* to the neighboring donor ion in ground state (D) such that the second ion ends in the identical excited state D^*. We called that process a donor-donor (D-D) transfer. This migration of the excitation over the donors changes the trapping efficiency since all excited donors, including those which are initially far away from any trap, can now transfer energy to donors which have traps as near neighbors. Figure 4 shows an example of CL and PL decay (shown as semilog plots) of $^3P_0 \rightarrow ^3F_2$ (653 nm) transitions at 12 K, with best fitting to double exponential decay for
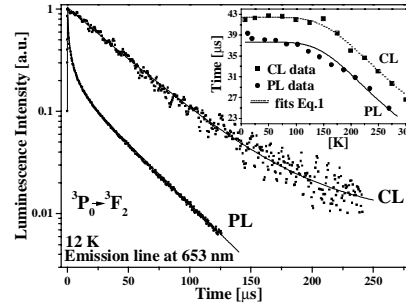

Fig.4 Luminescence decay observed from GaN: Pr^{3+} after N_2 laser pulse exc. (PL) and electron pulse exc. (CL) at 653 nm. Inset shows temperature dependence of $^3P_0$ decay time (■●) fitted to Eq.1 (doted, solid lines).

CL (solid line). Generally the decay times for transition $^3P_0 \rightarrow ^3F_2$ for CL and PL are 42 µs and 38.9 µs respectively, with little change with temperature as can be seen from inset in Fig. 4 .The CL and PL decay kinetics of the $^3P_1 \rightarrow ^3H_5$ at 522 nm, $^3P_0 \rightarrow ^3F_2$ at 653 nm, $^3P_1 \rightarrow ^3F_3$ at 673 nm, $^3P_0 \rightarrow ^3F_4$, at 755nm, $^3P_0 \rightarrow ^1G_4$ at 913nm and $^1D_2 \rightarrow ^3F_3$ at 956 nm emissions have been measured and the experimental results of the decay time data are summarizes in table I for temperatures 12 K and 300 K. The early time part of PL decay curve in Fig.4 from (and seems to be true for all investigated PL lines) is one exponential while the late- time

TABLE 1. CL and PL decay times of GaN:Pr³⁺

λ	Transition	CL decay time µs		PL decay time µs	
		12 K	300 K	12 K	300 K
522 nm	$^3P_1 \rightarrow ^3H_5$	33.6	----	----	----
653 nm	$^3P_0 \rightarrow ^3F_2$	42.0	27.8	38.9	40.6
670 nm	$^3P_1 \rightarrow ^3F_3$	43.0	29.5	36.4	15.4
755 nm	$^3P_0 \rightarrow ^3H_4$	----	----	27.0	10.8
913 nm	$^3P_0 \rightarrow ^1G_4$	46.5	33.6	39.9	48.0
956 nm	$^1D_2 \rightarrow ^3F_3$	46.3	27.7	----	----

luminescence decay is exponential with radiative decay time $\tau_o = 38.9$ µs suggesting that some of the Pr^{3+} ions are suggesting that some of the Pr^{3+} ions are in very isolated sites, or otherwise the cross relaxation between them is not allowed. The exponential component extracted from the experimental PL decay data of emission line at 653 nm portrayed for selected tempratures in inset Fig.4 is a radiative decay time τ_0 attributed to Pr^{3+} ions from isolated sites. The decay times τ of Pr^{3+} luminescence at 653 nm, is found to obey the activation formula in temperature range from 12 K to 270 K:

$$\frac{1}{\tau} = \frac{1}{\tau_0} + \beta \exp\left[\frac{-\Delta E}{kT}\right] \qquad (1)$$

where τ_0 is assumed to be the low temperature decay time and ΔE is the activation energy. The values obtained from the best fit (solid line in inset of Fig. 4) to the PL data are: $\tau_0 = 37.56$ μs, $\beta = 2.39 \times 10^5$ s^{-1} and $\Delta E = 533$ cm^{-1}, and for CL $\tau_0 = 42.4$ μs, $\beta = 1.2 \times 10^5$ s^{-1} and $\Delta E = 540$ cm^{-1} respectively (the ΔE is close to GaN TO phonon). The difference between CL and PL decay kinetics are probably related to different excitation processes and different centers involved in CL and PL emission (more experimental data and detailed analysis will be published elsewhere).

CONCLUSIONS .

In summary, it was demonstrated, that rare earth Pr^{3+} ions implanted into GaN after post-implantation isochronal annealing at 1100^0 C in N_2, at atmospheric pressure can be activated as luminescent centers emitting in the near UV, visible, and near infrared regions. The sharp characteristic emission lines corresponding to Pr^{3+} intra-4f^n-shell transitions are resolved in the spectral range from 350 nm to 1150nm, and observed over the temperature range of 12 K - 335K. The fluorescence decay curves of $^3P_1$, $^3P_0$ and $^1D_2$ levels emission were studied as a function of temperature. From this the characteristic time of the exponential decay of $^3P_0 \rightarrow {}^3F_2$ transition was determined Strong luminescence observed at low and room temperature using above bandgap photo excitation and electron beam, suggested that Pr in GaN can be effectively excited by forward bias p-n junction end utilized in LED and semiconductors lasers.

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