Optical transitions in Pr-implanted GaN

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Photoluminescence (PL) spectroscopy has been used to investigate praseodymium (Pr) related transitions in Pr-implanted GaN. Wurtzite GaN epilayers were grown by metalorganic chemical vapor deposition on sapphire substrates and subsequently ion implanted with Pr to a dose of $5.7\times10^{13}/\mathrm{cm}^2$. The implanted samples were annealed in nitrogen to facilitate recovery from implantation related damage. Narrow PL emission bands related to $4f$ intrashell transitions of the trivalent Pr ion were observed near 650, 950, 1100, and 1300 nm. The dependence of PL emission on sample temperature, excitation intensity, oxygen incorporation, and annealing temperature was systematically studied. We find that the PL efficiency increases exponentially with annealing temperature up to the maximum temperature of 1050 °C applied in the current study. Furthermore, the PL emission shows no evidence of significant thermal quenching over the sample temperature range of 10–300 K. This thermal stability will have particular advantages for applications in high temperature optoelectronic devices. © *1999 American Institute of Physics.*
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Rare earth doped glasses and insulating crystals have been extensively studied and developed for laser applications.[1] More recently, there has been considerable research effort involving the incorporation of rare earth elements into semiconductor hosts,[2–16] because such materials are of wide potential use in optoelectronic devices. Erbium (Er) and praseodymium (Pr)-doped materials are of particular interest to the optical communications industry because they exhibit emission at the wavelengths corresponding to the minimum transmission loss and minimum dispersion region within optical fibers, 1540 and 1300 nm, respectively. Studies of Er doped semiconductors have shown that thermal quenching of Er^{3+} emission decreases with increasing band gap of the host material.[5] This phenomenon has naturally led recent research efforts toward rate earth doping within the wide band gap III–nitride semiconductor system.[9–16] Recently, Pr has been incorporated into molecular beam epitaxy (MBE) grown GaN films by *in situ* doping as well as by focused ion beam implantation, and the feasibility of wavelength-specific visible light emission based on the rare earth incorporated GaN has been demonstrated.[15,16] This makes the fabrication of a full-color display from a single GaN chip possible.

In this work, we have incorporated Pr into metalorganic chemical vapor deposition (MOCVD) grown GaN films by the normal ion-implantation process. Photoluminescence (PL) spectroscopy has been employed to study the Pr-implanted GaN epilayers. Emission lines near 650, 950, 1100, and 1300 nm have been observed. The approximately 0.8 μm thick GaN films used for Pr ion implantation were grown by MOCVD on *c*-plane sapphire substrates. Details of the MOCVD growth are described elsewhere.[17] Pr was ion implanted into the GaN epilayers at a dose of $5.7\times10^{13}/\mathrm{cm}^2$ and energy of 300 keV. Figure 1 shows the SIMS profile of Pr in the Pr-implanted GaN film. Some GaN epilayers were implanted with both Pr and O at similar doses. After implantation, the samples were cut into small pieces that were annealed for 10 min in a nitrogen ambient at various temperatures ranging from 750 to 1050 °C. PL spectroscopy measurements were then performed on the Pr-implanted GaN samples. The excitation source consisted of 290 nm laser pulses with 10 ps width and 9.5 MHz repetition rate. The PL emission in the 650 nm wavelength region was collected and analyzed with a 1.3 m grating monochromator equipped with a microchannel plate photomultiplier tube used in a single photon counting mode. PL emission at wavelengths longer than 800 nm was collected and analyzed with a 0.3 m monochromator equipped with a thermoelectrically cooled InGaAs photodiode detector.

Figure 2 shows room temperature and 10 K PL spectra over the range of 640–680 nm for a Pr-implanted GaN sample annealed at 1050 °C. At least five distinct transitions can be seen in the spectra and the room temperature linewidths are clearly much smaller than expected for typical band or impurity related transitions of a semiconductor. Furthermore, the lines show virtually no temperature related wavelength shift as one might expect for band or impurity related transitions in semiconductors. These narrow PL emission lines appear related to $4f$ intrashell transitions of the Pr^{3+} ion. Similar visible-red Pr^{3+} emission was observed in recent studies where Pr was incorporated into GaN films by *in situ* doping and by focused ion beam implantation.[15,16] Comparison of the line positions with an energy diagram for Pr^{3+} indicates that the likely transition corresponding to the

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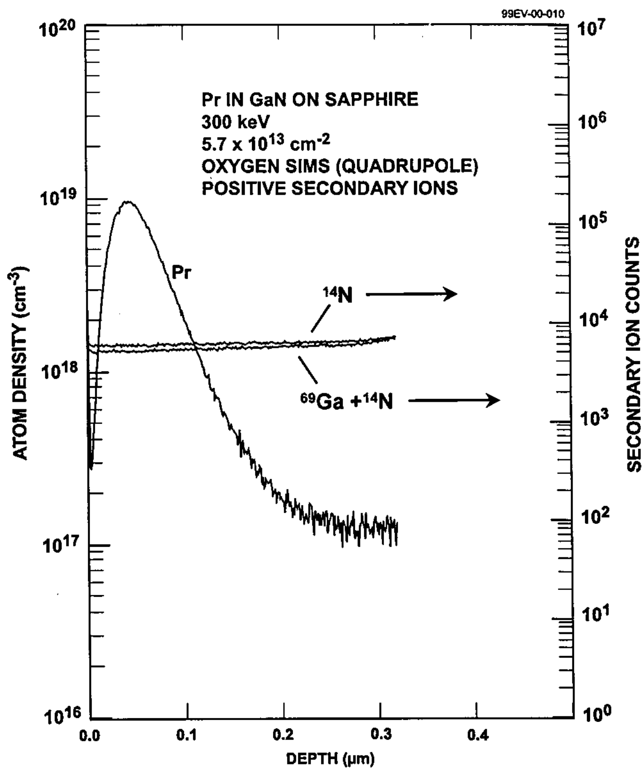

FIG. 1. SIMS profile of Pr in the Pr-implanted GaN film.

650 nm emission is $^3P_0-^3F_2$.[1] The closely spaced multiplet of lines originate from the crystal field splitting of otherwise forbidden transitions. The transition line at 646 nm in Fig. 2 is observable at 300 K but does not appear in the 10 K spectrum. This behavior is indicative of a ''hot line'' associated with a higher energy level of the multiplet only thermally populated at higher temperatures.[7]

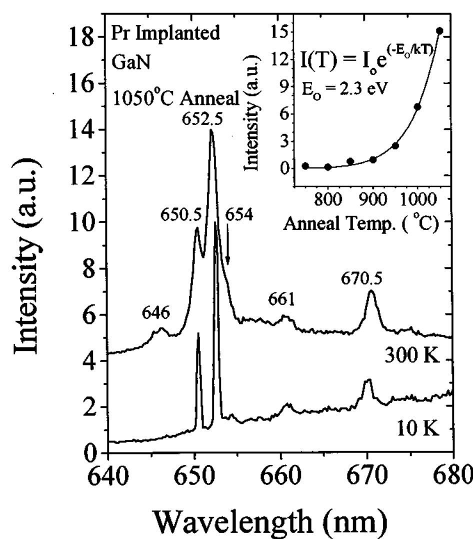

FIG. 2. PL spectra measured at 10 and 300 K from the Pr-implanted GaN sample annealed at 1050 °C. The spectra are vertically displaced for a clear presentation. The spectra show $^3P_0-^3F_2$ transitions of the Pr^{3+} ion in GaN near 650 nm. The inset shows the dependence of the integrated room temperature PL emission between 647.5 and 655 nm on sample annealing temperature.

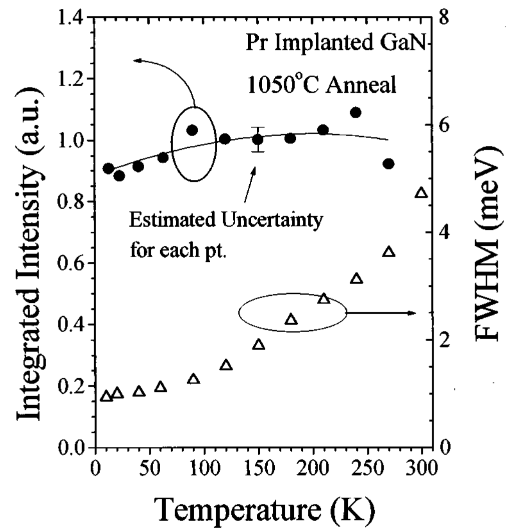

FIG. 3. Temperature dependence of the integrated PL intensity between 648 and 656 nm (solid circles) and linewidth (open triangles) of the 652.5 nm peak. The data shown is for the Pr-implanted sample annealed at 1050 °C.

The PL emission from the Pr-doped samples exhibited a strong dependence upon sample annealing temperature. The inset of Fig. 2 shows the integrated PL intensity as a function of annealing temperature for the most intense pair of transitions at 650.5 and 652.5 nm. We find the PL intensity increases exponentially with annealing temperature up to the highest temperature of 1050 °C used in this study. A least squares fit of exponential form implies a thermal activation energy of 2.3 eV for the Pr-implanted GaN. We did not attempt to anneal at any temperature higher than 1050 °C in this study. However, the data shown in the inset of Fig. 2 indicate that Pr^{3+}-related PL efficiency will continue to increase with higher anneal temperature until a point where thermal degradation of the GaN host material becomes prevalent or a point of complete Pr^{3+} activation. The study by Chao and Steckl showed that the Pr-related PL efficiency increases with increased annealing time for a fixed temperature of 950 °C.[16] The GaN band edge PL near 3.4 eV at room temperature (not shown) was also studied for the Pr-implanted samples annealed at various temperatures. However, very little band edge PL could be detected and the PL intensity did not follow any obvious trend with annealing temperature.

Figure 3 shows the dependence of the Pr^{3+} emission on sample temperature for the Pr-implanted sample annealed at 1050 °C. The integrated PL intensity between 648 and 656 nm is shown with solid circles. The data have been smoothed by a three point running average in order to reduce systematic scatter and the error bar represents an estimate of the uncertainty associated with each plotted point. The solid line in Fig. 3 is included as an aid to the eye. It is clear from Fig. 3 that there is no significant thermally induced degradation of PL efficiency up to room temperature. Although the integrated PL intensity is quite stable with temperature, the transition linewidth does exhibit thermal broadening as seen in Fig. 2. The data in Fig. 3 indicated by open triangles represent the measured full width at half maximum for the 652.5 nm transition. We see that the linewidth increases from 0.9

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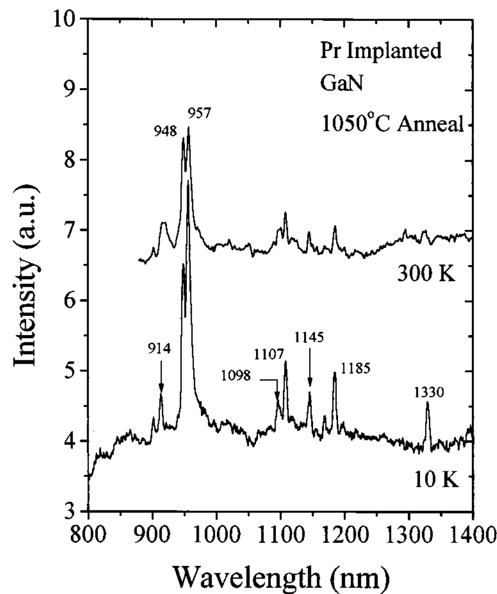

FIG. 4. Infrared PL emission spectra measured at 10 and 300 K from the Pr-implanted GaN sample annealed at 1050 °C. The spectra are vertically displaced for a clear presentation. Transitions were observed near 900–1000, 1100–1200, and 1330 nm.

meV at a sample temperature of 10 K to 4.7 meV at a temperature of 300 K. It should be noted that there is an approximate 0.46 meV (at 652 nm) contribution to the observed linewidths due to the monochromator slit width.

Some of the GaN samples of the current study were implanted with both Pr and O in order to investigate the effect of oxygen impurities on the Pr^{3+}-related PL efficiency. These samples were annealed at various temperatures in a manner identical to the annealing process used for the GaN samples solely doped with Pr. We found that at all annealing temperatures investigated, the Pr+O doped samples exhibited less PL intensity near 650 nm than the samples doped with only Pr. Using samples annealed at 1000 °C, for example, the integrated PL intensity from the Pr+O sample was only 45%–50% of that observed from the Pr doped sample. It is interesting to compare our results to early studies of Er-doped semiconductors, which suggested that oxygen incorporation can enhance the Er^{3+} PL efficiency.[5,6,9] Rather than observing such an oxygen related enhancement, when optically pumped at an energy above the band gap of GaN, we observe a modest degradation of Pr^{3+}-related PL efficiency. Our results corroborate a recent study[18] where little Er^{3+} PL efficiency dependence on oxygen codoping was seen in Er-doped GaN under an above band gap excitation condition.

In addition to the Pr^{3+} transitions recorded in the visible spectrum, PL emission was observed in the infrared wavelength region. Figure 4 shows 10 and 300 K PL spectra from 880 to 1400 nm for the Pr-implanted sample annealed at 1050 °C. Here, three sets of emission peaks are observed in the wavelength regions 900–1000, 1090–1200, and 1330 nm, respectively. These transitions were also recently observed from MBE grown GaN doped *in situ* with Pr.[15] According to an energy diagram for Pr^{3+}, the 900–1000 nm peaks are most likely due to crystal field-split ${}^1D_2-{}^3F_3$ transitions,[1] while those in the 1090–1200 nm range are not clearly identified. The Pr^{3+} emission relevant to the optical communications industry, near 1.33 μm, was observed within the 10 K spectrum but was weaker than the shorter wavelength transitions. At the sample temperature of 300 K, the 1.33 μm transition is obscured by the background and noise level of the spectrum.

In summary, Pr has been incorporated into GaN epilayers by ion implantation. Pr^{3+}-related PL was observed from these samples, and the efficiency of the PL increased exponentially with postimplantation anneal temperature, indicating a thermal activation behavior with a characteristic energy of $E=2.3$ eV. Narrow PL emission lines associated with the Pr^{3+} centers were observed near 650, 950, 1100, and 1300 nm. The 650 nm emission was studied as a function of sample temperature and the integrated PL intensity was found to be very stable with temperature. In contrast to studies of Er-doped GaN, the addition of oxygen impurities to the Pr-implanted samples resulted in lower PL efficiency for all of the annealing temperatures studied. This work demonstrates that Pr^{3+}-related emission can be obtained from wurtzite GaN ion implanted with Pr, and proper choice of annealing parameters may maximize this emission for device applications such as electrically pumped optical amplifiers, light emitting diodes, or laser diodes that emit at spectrally narrow Pr^{3+} lines.

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