Red light emission by photoluminescence and electroluminescence from Pr-doped GaN on Si substrates

R. Birkhahn, M. Garter, and A. J. Steckl[a)]
Nanoelectronics Laboratory, University of Cincinnati, Cincinnati, Ohio 45221-0030

(Received 9 September 1998; accepted for publication 12 February 1999)

Visible light emission has been obtained at room temperature by photoluminescence (PL) and electroluminescence (EL) from Pr-doped GaN thin films grown on Si(111). The GaN was grown by molecular beam epitaxy using solid sources (for Ga and Pr) and a plasma gas source for N_2. Photoexcitation with a He–Cd laser results in strong red emission at 648 and 650 nm, corresponding to the transition between $^3P_0$ and $^3F_2$ states in Pr^{3+}. The full width at half maximum (FWHM) of the PL lines is ~1.2 nm, which corresponds to ~3.6 meV. Emission is also measured at near-infrared wavelengths, corresponding to lower energy transitions. Ar laser pumping at 488 nm also resulted in red emission, but with much lower intensity. Indium-tin-oxide Schottky contacts were used to demonstrate visible red EL from the GaN:Pr. The FWHM of the EL emission line is ~7 nm. © *1999 American Institute of Physics.* [S0003-6951(99)00315-0]

Since the initial development of GaN optoelectronic technology starting approximately a decade ago, the push for blue light emitting devices (LEDs) and lasers has continued unabated and great progress has been made.[1–4] A series of technical issues remain to be resolved[5] in LED fabrication and manufacturing, including the complexity of integrating different materials systems (e.g., InGaN for blue and AlInGaP for red LEDs), difficulty with the AlGaN properties as cladding, and compensating for different performance characteristics such as current and voltage requirements. An alternative approach is to utilize a single GaN host doped with several light-emitting rare earths (REs). This approach can simplify the LED structure and, hence, the fabrication processes and reduces cost by utilizing a common semiconductor host. By introduction of Pr^{3+} for red, Er^{3+} for green, and another RE for blue, a full-color display can be fabricated from a single substrate. Based on currently known properties[6] of REs, we suggest Tm^{3+} or Ce^{3+} could produce the desired blue emission.

Rare earths introduced into III–V compound semiconductors by molecular beam epitaxy (MBE) had resulted in the first report[7] of strong infrared (IR) photoluminescence (PL) at room temperature (Er in GaAs emitting at 1.54 μm). MBE growth of GaN on Si has been reported[8] and MBE has been successfully used[9] to fabricate GaN p-n junction LEDs, leading to the use[10] of MBE for growing *in situ* Er-doped GaN.

Recently, we have reported[11,12] the successful *in situ* incorporation of the RE Er into GaN by MBE on both sapphire and silicon, producing room temperature visible and IR emission by both PL and electroluminescence (EL). In GaN:Er, besides the commonly measured 1.5 μm emission, we observed two narrow and very strong green lines at 537 and 558 nm, corresponding to higher level Er^{3+} transitions. In this letter, we report on Pr-doped GaN growth on Si(111) substrates and the resulting IR and novel visible red emission at 650 nm, not previously observed outside of glass hosts. Spectroscopically, these specific RE atomic levels in the visible region for $Pr^{3+}(^3P_0)$ and $Er^{3+}(^2H_{11/2}, {}^4S_{3/2})$ are both known to have high likelihood of transition.[13] However, for reasons not yet clear, they are not readily observed when these REs are doped into other III–V, IV, or II–VI semiconductor hosts. The only known system[14–17] in which RE-doped semiconductors emit in the visible is ZnSe:Er. Pr has been implanted into GaAs,[18,19] AlGaAs,[20] and GaP[21–23] but the only emission reported has occurred at IR wavelengths. Our work demonstrates the feasibility of wavelength-specific *visible* light emission based on the RE species incorporated into GaN.

Pr-doped GaN films were grown in a Riber MBE-32 system on 2 in. (50 mm) p-Si(111) substrates. Solid sources were employed to supply the Ga and Pr fluxes, while a SVTA radio frequency (rf)-plasma source was used to generate atomic nitrogen. The growth of GaN:Pr followed the procedure previously reported[11] for GaN:Er. Substrate growth temperature was kept constant at 750 °C and the Pr cell temperature was 1200 °C. We estimate, based on our work with GaN:Er, that this cell temperature results in a Pr concentration in the range of 10^{18}–10^{20}/cm^3. PL characterization was performed with He–Cd and Ar laser excitation sources at wavelengths of 325 and 488 nm, respectively. The PL and EL signals were characterized with a 0.3 m Acton Research spectrometer outfitted with a photomultiplier tube detector for ultraviolet-visible wavelengths and an InGaAs detector for IR. To measure EL characteristics, contacts were formed by sputtering a transparent and conducting indium-tin-oxide (ITO) layer onto the GaN:Pr structure.

He–Cd PL excitation (at 325 nm) resulted in an intense, deep red emission from the Pr-doped GaN, visible with the naked eye. The room temperature PL at visible wavelengths is shown in Fig. 1 for a 1.5-μm-thick GaN film grown on Si. The spectrum indicates a very strong emission line in the red region at 650 nm, with a weak secondary peak at 668 nm. As discussed in more detail below, we assign the dominant emission to the transition between the $^3P_0$ and $^3F_2$ states of

a)Electronic mail: a.steckl@uc.edu

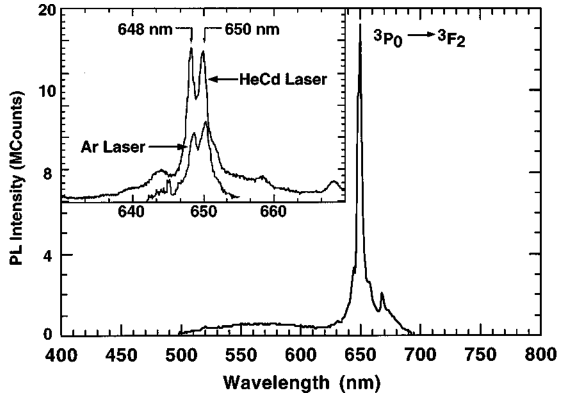

FIG. 1. Room temperature PL spectra of Pr-doped GaN films grown on Si (111). The PL is performed with a He–Cd laser line at 325 nm. Insert contains high resolution scans of the $^3P_0 \rightarrow {}^3F_2$ transition of Pr^{3+} at 650 nm performed with the He–Cd and Ar (at 488 nm) lasers.

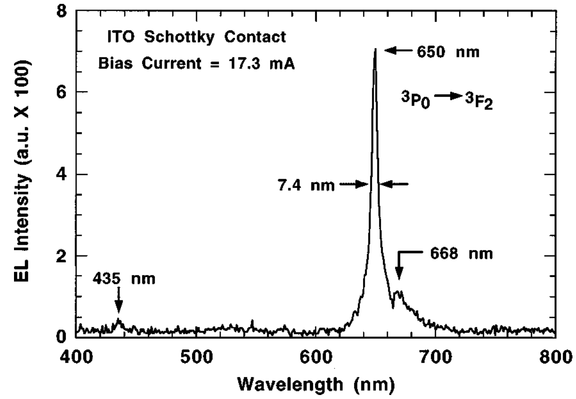

FIG. 3. Visible EL spectrum from ITO Schottky contact on GaN:Pr layer. The bias current is 17.3 mA at a voltage of 144 V.

Pr^{3+}. This dominant $^3P_0 \rightarrow {}^3F_2$ transition was also reported in Pr-doped ZBLAN glass.[24] The Pr emission lines are superimposed on a broad and weak GaN emission background, which peaks in the yellow at around 560 nm. As shown in the inset of Fig. 1, Stark splitting of the levels involved in the main transition results in two closely spaced red emission lines, with wavelengths of 648.25 and 649.9 nm. The full width at half-maximum (FWHM) of each of these two main components is ~1.22 nm, which corresponds to an energy width of ~3.6 meV. For this measurement the resolution of the spectrometer was 0.08 nm. Minor peaks located at 630, 644, 658.3, and 668.3 nm are also present.

Ar laser excitation (at 488 nm) also resulted in visible emission (included in Fig. 1 inset) with a similar doublet at 648 and 650 nm, although not nearly as intense as the PL produced by He–Cd excitation. Minor peaks in the spectrum were not as clear due to multiple laser lines and emission from the Si substrate.

The GaN:Pr PL spectrum at near-IR wavelengths under He–Cd excitation is shown in Fig. 2. Four different regions of optical activity can be seen in the region from 800 to 2000 nm. The first set of lines contains the strongest IR peak at 960 nm with a secondary line at 920 nm. The second multiplet has four emission peaks of roughly the same intensity at 1095, 1110, 1140, and 1190 nm. The third group consists of just one peak at 1303 nm corresponding to the commonly observed $^1G_4$ transition to the $^3H_5$ state. One should note that this peak is the least intense of the IR series. The final pair of IR peaks is present at 1895 and 1915 nm. Similar to the visible lines, the IR peaks are also quite narrow. For example, the longest wavelength peak detected at 1915 nm has a FWHM of ~16 nm, which corresponds to an energy width of ~5.4 meV. No emission in the IR could be detected under Ar laser excitation. The signal may have been too weak to be measured by the InGaAs detector.

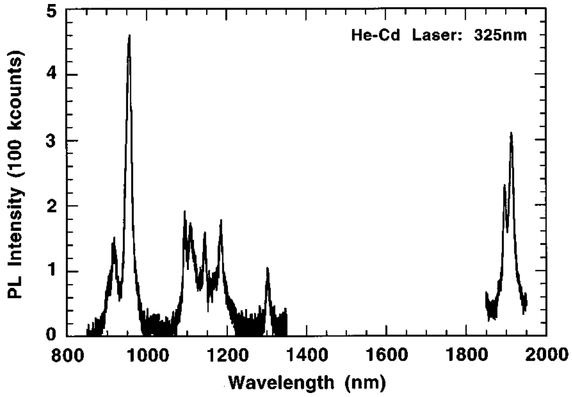

FIG. 2. Infrared spectrum of GaN:Pr taken at room temperature with excitation by He–Cd laser at 325 nm.

Preliminary results on EL from GaN:Pr films were obtained by fabricating Schottky diodes. Transparent electrodes of unequal sizes were fabricated utilizing ITO films deposited by rf sputtering. Red light emission was observed at room temperature as direct current reverse bias was applied to the diode. Figure 3 shows the visible EL spectrum from a GaN:Pr Schottky diode with area of $7.65 \times 10^{-4}\,cm^2$ operated with a bias current of 17.3 mA at 144 V. The main emission is a single peak at 650 nm with a FWHM of 7 nm, corresponding to the same $^3P_0 \rightarrow {}^3F_2$ transition observed under laser excitation. In the EL case we did not observe the splitting of this transition, which was observed during PL. A second EL peak is present at 668 nm and a very weak third peak appears at ~435 nm.

To identify the origin of the PL and EL peaks in GaN:Pr we have utilized the well-known optical characteristics[25] of $LaCl_3$:Pr. Figure 4 contains the reported Pr inner shell energy levels (shown in italics) in $LaCl_3$. The width of each level indicates qualitatively the energy spread present. Also indicated in Fig. 4 are the energies of the excitation photons from the He–Cd and Ar lasers, and the lower edge of the GaN conduction band. Finally, the main optical emission lines observed from GaN:Pr are shown associated with specific Pr transitions. As indicated above, the red emission dominating visible PL and EL is caused by the $^3P_0 \rightarrow {}^3F_2$ transition. The emitted photon energy of ~1.91 eV for this transition matches well the 1.927 eV value reported for Pr-doped $LaCl_3$. The first major IR peak observed at 956 nm (or an energy of 1.297 eV) is assigned to the $^1D_2 \rightarrow {}^3F_3$ transition. The corresponding energy for this transition in $LaCl_3$ is 1.289 eV. As shown in Fig. 2, assignments for all but two of the minor peaks were obtained with fairly good agreement.

In summary, we have reported optical emission characteristics of Pr-doped GaN on Si(111) grown by solid source MBE. We have observed for the first time visible emission from the Pr-doped semiconductor thin films. In conjunction

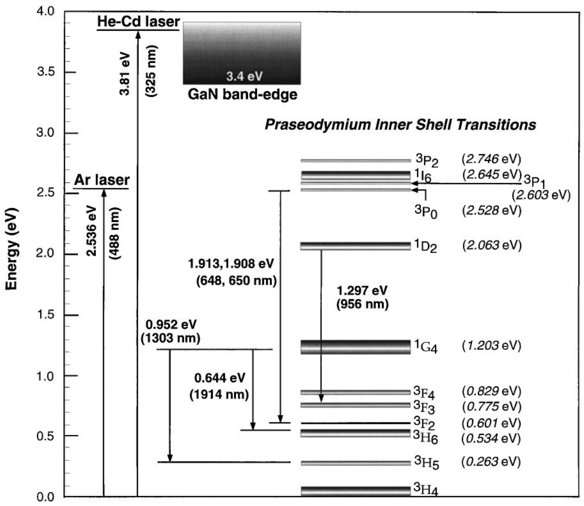

FIG. 4. Energy band diagram of Pr-doped GaN. The energy levels of the Pr states (in italics) correspond to values reported for $LaCl_3$:Pr. The wavelengths and energies shown for transitions between Pr levels are experimentally measured in GaN:Pr. Also shown are the photon energies of the He–Cd and Ar lasers.

with our previous work with Er, wide-band gap GaN is seen to provide a suitable environment to elicit the higher energy atomic transitions corresponding to visible wavelengths in rare earth dopants. As a result, we predict a wide array of colors from different rare earths can be realized. The use of Si substrates for growth of GaN doped with Pr and Er indicates the possibility of future integration with Si device technology.

This work was supported by a BMDO/ARO contract (L. Lome and J. Zavada) and an ARO AASERT grant. The authors would like to acknowledge many technical discussions and the support and encouragement of J. Zavada. Equipment support was provided by an ARO URI grant and the Ohio Materials Network.

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