

Luminescence dynamics and waveguide applications of europium doped gallium nitride powder

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The authors present time resolved photoluminescence studies of the 621 nm emission of Eu doped GaN in the form of a powder. The authors also show light guiding on chip using SiON waveguides in conjunction with the GaN powder. The Eu luminescence shows two distinct temperature dependent behaviors of the lifetime when excited above the GaN band gap, one at 185 K and one at 104 K, with corresponding activation energies of 16 and 9 meV, respectively. © 2006 American Institute of Physics. [DOI: 10.1063/1.2338894]

Rare earth (RE) doped GaN compounds have been attracting much attention in recent years.¹⁻⁴ Lasing of Eu doped GaN has also been recently demonstrated.⁵ The relatively large band gap of GaN enables strong emission from the RE ions within it, partly because of reduced thermal quenching which decreases with the band gap energy of the host semiconductor material.⁶ This emission (with GaN or other semiconductors as host materials) can be made useful in applications such as optical fiber amplifiers, lasers, and electroluminescent devices, for example.⁷ Using RE doped semiconductors as phosphors also opens the possibility for displays.²

The vast majority of the reported RE doped semiconductor materials and their applications rely on fabrication that involves molecular beam epitaxy (MBE).^{1-4,7,8} Sputtering,⁹ metal organic chemical vapor deposition (MOCVD),¹⁰ and hybrid vapor phase epitaxy¹¹ are also reported as growth techniques. Ion implantation of Eu ions into MOCVD grown GaN is another alternative.¹² All of these film deposition growth methods result in films that are limited to the substrate onto which they are grown. The powder form of the GaN:Eu studied in this letter is obtained from a high yielding, highly repeatable process, as previously reported for the case of GaN:Er.^{13,14} Other methods of obtaining a powder form of RE doped GaN involve a combustion reaction¹⁵ or an ammonolysis of freeze-dried precursors.¹⁶ The powder form offers the possibility of hybrid-type integrated photonic structures, bestowing optical properties to optically inactive materials in a spin-on process, for example.

The main steps in the fabrication of the GaN:Eu powder involve heating at 830 °C for several hours and cooling a mixture of gallium, bismuth shot, and europium ingot in an ammonia ambient to initially obtain chunks of the desired material.^{13,14} The cooled chunks are then manually ground into a fine powder using a mortar and pestle, and the bismuth is removed by heating the material for several hours at 1030 °C under flowing NH₃. The resulting material is a highly pure and crystalline versatile powder as confirmed by x-ray diffraction measurements. As was previously reported in the case of GaN:Er powder,¹⁴ an x-ray diffraction spectrum was obtained showing no presence of Bi following the evaporation step. The powder can be combined with cellu-

lose to obtain a mélange which can be easily spun into a thin film onto any substrate. The sample used for the lifetime measurements was created by spin coating a Si substrate with this mix of 1 at. % Eu doped GaN to obtain a thin film of approximately a few micrometers thick. The cellulose is easily baked off with a moderate temperature anneal. Similar photoluminescence (PL) spectra were obtained from the spun coated sample compared to freestanding powder.¹⁷

Time resolved photoluminescence (TRPL) measurements were performed on the 621 nm emission of the GaN:Eu powder. Figure 1(a) shows a PL spectrum obtained from the thin film of GaN:Eu spun onto the Si substrate, obtained using a HeCd laser (325 nm). A pulsed N₂ laser (337.1 nm) with <4 ns pulse width, at a repetition rate of 29 Hz with pulse energy of approximately 2 μJ/cm², was used for the lifetime measurements, and the time signals were measured with a spectral window of 4.5 meV centered on the 621 nm line using a photomultiplier tube. A liquid nitrogen cooled cryostat was used in order to perform temperature dependent measurements, from 80 K to room temperature.

Figure 1(b) shows a lifetime decay curve of the 621 nm line obtained at room temperature, along with a double exponential fit following the equation:

$$I(t) = A_S e^{-t/\tau_S} + A_F e^{-t/\tau_F}, \quad (1)$$

where the subscripts *S* and *F* refer to the slow and fast components, respectively. One can see that the emitter (Eu³⁺) undergoes a fast initial decay on the order of a few tens of

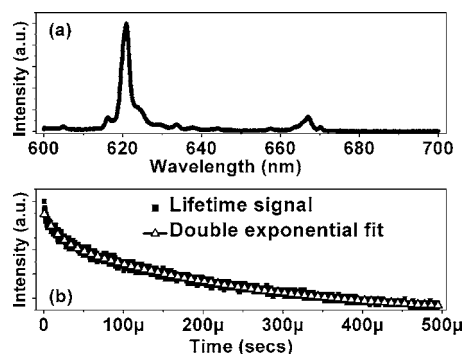


FIG. 1. (a) PL spectrum of the GaN:Eu under HeCd (325 nm) excitation at room temperature. (b) Experimental lifetime decay curve (solid squares) of the 621 nm line with double exponential fit (triangles).

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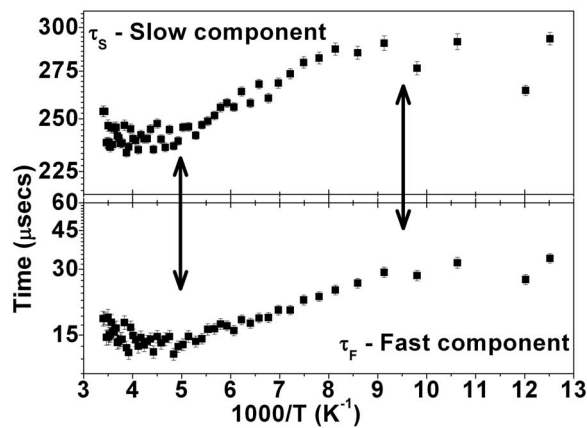


FIG. 2. Lifetimes obtained from best fits of Eq. (1) to the curves obtained from TRPL of the GaN:Eu powder at 1 at. % Eu.

microseconds, followed by a slower decay on the order of a few hundreds of microseconds. The faster decay component is associated with additional nonradiative decays to those of the slower decay component, the latter involving temperature insensitive radiative and temperature sensitive nonradiative decays.^{18,19} Figure 2 shows the temperature dependence of the fast and slow lifetime components of the powder obtained using Eq. (1). A clear increase of both of the lifetime components with a decrease of temperature is evident, indicating that, at higher temperatures, nonradiative decay mechanisms clearly affect the decay of the Eu^{3+} .

A closer look at the curves shown in Fig. 2 reveals that there are two temperatures at which a clear change of both lifetime components occurs, indicated by the arrows. These changes signify that there may be two impurity levels below the GaN band gap that contribute to the Eu emission, one at about 9 meV ($T=104$ K) and the other at an activation energy of 16 meV ($T=185$ K). Note that no significant change in the radiative lifetime is observed for temperatures above 185 K. This temperature dependence of the lifetime is in strong contrast to the MBE grown crystalline GaN:Eu in bulk form,¹⁸ in which a single temperature dependent impurity was shown to contribute to the Eu decay, and a strong change in the decay rates is observable at high temperatures. For comparison, the slow and fast lifetime components at room temperature reported here are 253 and 18 μs , respectively, compared to ~ 200 and ~ 35 μs for bulk MBE GaN:Eu.¹⁸

A distinct advantage of the powder form of RE doped GaN compared to a substrate-dependent MBE grown similar material is that the powder can be easily used as a coating active material, effectively rendering optical properties to inert materials. The recent demonstration of a laser in Si waveguides using a vertically offset active layer of Al-GaNAs quantum wells shows the promise of the heterogeneous combination.²⁰

We used a cellulose GaN:Eu dispersion to spin coat a thin layer of the powder onto visible wavelength guiding SiON waveguides, followed by a calcination to remove the cellulose. The SiON waveguides were fabricated on a silicon wafer on which a 5 μm SiO_2 optical buffer layer was deposited using plasma enhanced chemical vapor deposition (PECVD), after which a 700 nm thick layer of PECVD SiON was deposited. This last layer was patterned using standard photolithography techniques: OiR-620-7i photore-

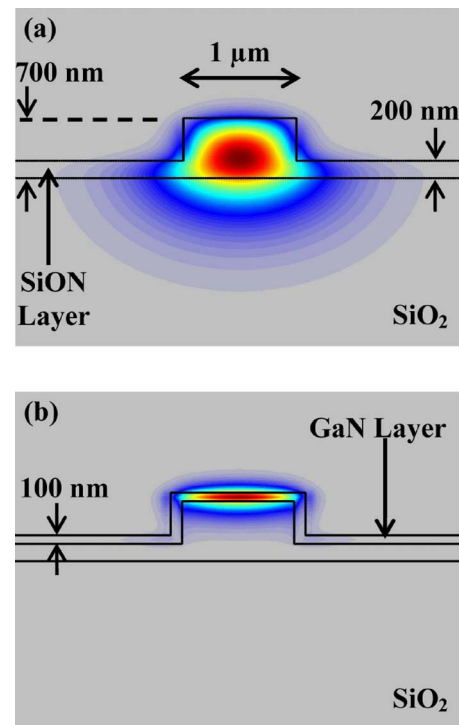


FIG. 3. (Color online) (a) Fundamental mode (TE-like) of the SiON waveguide at 621 nm, assuming $n=1.53$. (b) Fundamental TE-like mode in the GaN film, assuming $n=1.53$ for the SiON and $n=2.3$ for the GaN.

sist was spin coated onto the wafer, then patterned and developed. Reactive ion etching in a CHF_3 ambient was used to etch the waveguides. The deposition conditions of the SiON layer were such as to obtain an index of refraction of 1.53 for the thin film.

A cross section of a SiON waveguide along with a plot of the simulated transverse electric (TE) fundamental mode (at a wavelength of 621 nm, electric field in the left-right orientation) using an index of refraction $n=1.53$ is shown in Fig. 3(a). The simulated fundamental TE mode of the chip covered with a smooth and uniform layer of GaN:Eu of 100 nm in thickness is shown in Fig. 3(b). Measurements of several SiON waveguides (without the GaN:Eu powder) with lengths varying from ~ 3.9 to ~ 7.7 mm resulted in propagation losses on the order of 26 dB/cm. The measurements were performed using the 457.9 nm line from an argon laser coupled into a single mode visible optical fiber. 300 μW of power was measured at the tapered end of the optical fiber. The tapered end of the optical fiber was used to couple the Ar light into the waveguides of the polished sample. The output of the waveguides was collected with an objective lens [0.55 numerical aperture (NA)] and sent onto a visible detector (Newport 818-SL). The presence of the GaN:Eu powder resulted in an increase of the propagation losses by approximately $8(\pm 2)$ dB/cm.

In conclusion, we have shown that GaN:Eu in the form of powder presents very similar time characteristics as previously measured for MBE grown GaN:Eu.¹⁸ We have also presented groundwork for the use of the RE doped GaN powder for the purpose of on-chip applications.

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