

Effect of Si codoping on Eu³⁺ luminescence in GaN

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Eu and Si codoped GaN thin films were grown on sapphire by solid source molecular beam epitaxy. Eu³⁺ photoluminescence (PL) emission at ~ 622 nm (5D_0 - 7F_2) was enhanced by approximately five to ten times with Si doping. The effect of Si codoping on PL intensity, lifetime, and excitation dependence revealed two distinct regimes. Moderate Si doping levels (0.04–0.07 at. %) lead to an increase in lifetime combined with improved excitation efficiency and a greatly enhanced PL intensity. High Si doping levels (0.08–0.1 at. %) significantly quench the PL intensity and lifetime, due primarily to nonradiative channels produced by a high defect population. © 2009 American Institute of Physics. [DOI: 10.1063/1.3077268]

Rare earth (RE) doped gallium nitride is being widely investigated^{1,2} for potential applications in semiconductor displays, light-emitting diodes, and lasers because RE ions can provide stable and sharp emissions from visible to infrared wavelengths. The incorporation of codopants along with RE elements in semiconductor hosts has been shown to have significant influence on RE luminescence.^{3–7} In this paper, we report on the strong effect on Eu red luminescence of Si codoping in GaN thin films.

Si and Eu codoped GaN thin films (GaN:Eu,Si) were *in situ* grown on *c*-plane (0001) sapphire wafers using a Riber 32 molecular beam epitaxy system. Sapphire wafers were first cleaned by a standard wet clean procedure and then degassed at 850 °C under $\sim 10^{-10}$ Torr vacuum. A N₂ gas flow rate of 2.2 SCCM (SCCM denotes cubic centimeter per minute at STP) was used in conjunction with a plasma rf power of 400 W. The sapphire wafers were nitridated in N₂ flow only at 850 °C for 10 min prior to growth. A 20 nm low temperature GaN buffer layer was followed by 1 h growth of Eu and Si codoped GaN at 800 °C. Ga was introduced from an effusion cell loaded with 6N Ga metal. The beam equivalent pressure was measured as $\sim 2.5 \times 10^{-7}$ Torr, where the growth condition was lightly N rich condition (III/V ratio < 1). Eu and Si were *in situ* codoped in GaN thin films using 3N Eu and 6N Si metals. The Eu cell temperature was maintained at 450 °C for all samples discussed. Si cell temperatures from 950 to 1200 °C were used to obtain different Si doping concentrations. The growth rate was ~ 0.45 $\mu\text{m/h}$. For comparison, GaN samples doped only with Eu were also grown under the same conditions.

The Eu atomic concentration in GaN thin films is typically ~ 0.10 – 1.00 at. %. The incorporation of Si atoms in the thin films competes with Eu incorporation since both are mostly located on substitutional Ga sites. Therefore, heavy Si doping is likely to affect the Eu concentration. The doping depth profiles in GaN:(Eu, Si) and GaN:Eu films were inves-

tigated by secondary ion mass spectroscopy (SIMS). The estimated Eu and Si atomic concentrations based on SIMS measurements are shown in Fig. 1 as a function of Si cell temperature. The hashed region shows the range of typical Eu concentration (~ 0.50 at. %) from GaN:Eu thin films on sapphire substrates under the same growth condition. As seen in Fig. 1, at low Si concentrations the Eu level in codoped GaN thin films is constant and similar to that of Eu-only GaN thin films. As the Si cell temperature reaches levels (~ 1100 °C) that produce Si concentrations of ~ 0.1 at. %, the Eu concentration incorporated into the GaN film begins a steady and significant decrease, reaching almost one-half of its initial value when Si cell temperature is 1200 °C. On the other hand, the Si concentration increases monotonically with the Si cell temperature. The rate at which the Si concentration increases is reduced at approximately the same Si cell temperature (~ 1100 °C) at which the Eu concentration begins to decrease. Normally, GaN:Eu thin films are quite electrically resistive. The Si codoping increases the electron concentration significantly.

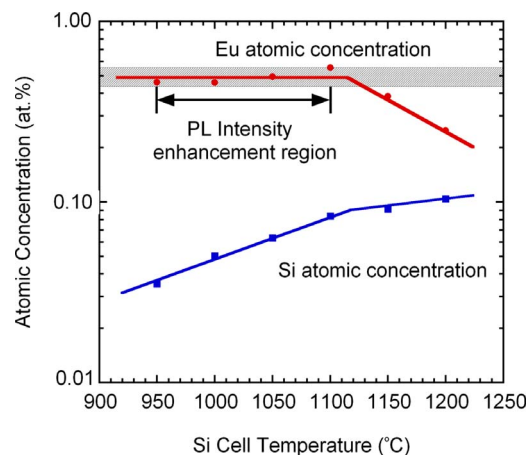


FIG. 1. (Color online) Eu and Si atomic concentrations estimated from SIMS measurements. Hashed region indicates the range of Eu concentration in GaN films, which are not Si co-doped.

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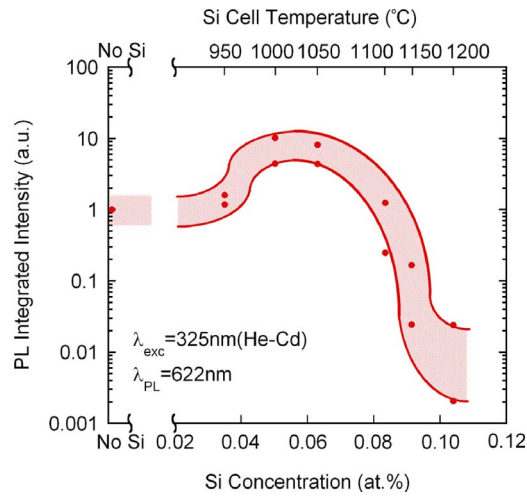


FIG. 2. (Color online) Integrated PL intensity at ~ 622 nm as a function of Si concentration using above-bandgap excitation.

The effect of Si codoping on Eu^{3+} red luminescence was first studied by room temperature “above-bandgap” excitation, using a 325 nm He–Cd UV laser. PL spectra of the codoped GaN:Eu,Si thin films with different Si doping concentrations show very strong red emission at ~ 622 nm from ${}^5D_0\text{--}{}^7F_2$ transitions of Eu^{3+} ions. Several weaker emission lines at ~ 600 nm (${}^5D_0\text{--}{}^7F_1$), ~ 663 nm (${}^5D_0\text{--}{}^7F_3$), and ~ 546 nm (${}^5D_1\text{--}{}^7F_1$) are also present. Figure 2 shows the strong effect of Si codoping on the red luminescence, where PL intensity (integrated over the ~ 622 nm red emission range) is plotted as a function of Si concentration and corresponding cell temperature. For comparison, the PL intensity range of GaN:Eu thin films is shown as the hashed bar on the left side of Fig. 2. At sufficiently low Si concentrations (~ 0.04 at. %), the PL intensity from GaN:Eu and GaN:Eu,Si films are very similar. As the Si cell temperature increased and more Si atoms are incorporated into GaN thin films, the Eu^{3+} emission intensity increased significantly. Approximately five to ten times PL increase was obtained for a Si concentration of ~ 0.05 at. % (Si cell temperature is between 1000 and 1050 °C). However, for Si concentrations higher than ~ 0.07 at. %, the emission intensity starts to decrease rapidly. When the Si cell temperature is ~ 1200 °C (resulting in a Si concentration of ~ 0.1 at. %), the PL emission is ~ 1000 times lower than its peak value. Clearly, the reduction in Eu emission is much stronger than the decrease in Eu concentration (approximately two times) over the entire Si concentration range.

In order to study more clearly the effect of Si codoping, time resolved PL experiments were performed. PL decay transients were recorded using an optical parametric oscillator system (repetition rate: 10 Hz, pulse width: 5–10 ns) operating at 471 nm for below-gap (resonant) pumping. The fourth harmonic output of a YAG:Nd laser at 266 nm was employed for above-gap pumping. Emission at ~ 622 nm was dispersed using a 0.3 m monochromator equipped with a photomultiplier tube for detection. Figure 3(a) shows PL decay transients from codoped GaN:Eu,Si thin films pumped at 266 nm. At moderate Si doping, the PL intensity shows a slower decay process than the PL from GaN:Eu thin films.

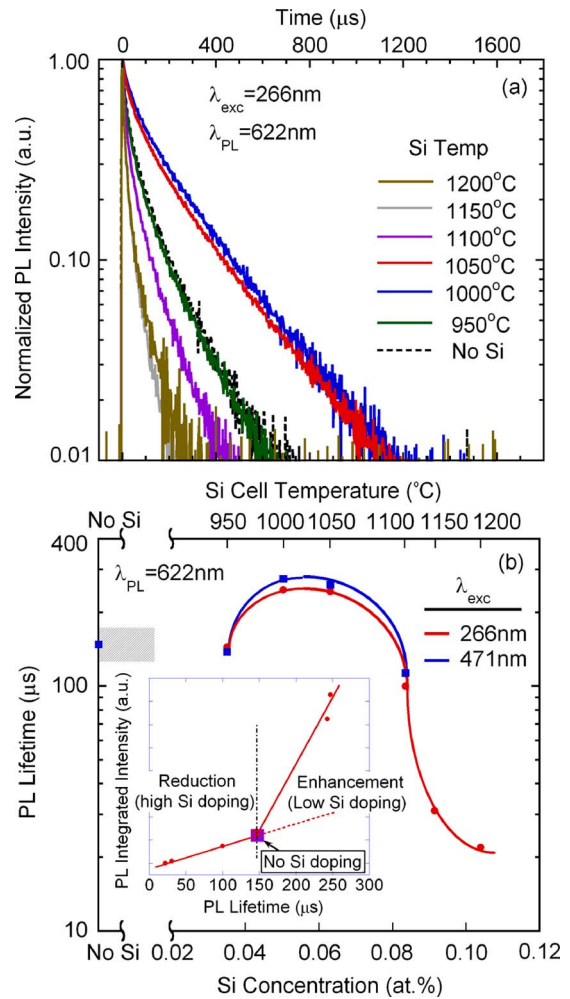


FIG. 3. (Color online) PL lifetime dependence on Si concentration excited at 266 nm (above bandgap) and 471 nm (below bandgap). (a) Normalized PL vs time. (b) Calculated PL lifetime vs Si concentration (insert shows PL intensity vs lifetime).

PL lifetimes were calculated and are plotted versus Si doping concentration in Fig. 3(b). The trend of PL lifetime dependence on Si doping concentration is similar but not identical to that of red PL intensity shown in Fig. 2. The insert in Fig. 3(b) shows that the PL intensity does not have a simple linear dependence on the lifetime.

PL excitation (PLE) of the luminescence at ~ 622 nm was investigated primarily covering the ${}^5D_0\text{--}{}^7F_0$ transition region. The PLE spectra were recorded using the tunable laser output ($\sim 565\text{--}595$ nm) from the narrow-band optical parametric oscillator (OPO) system (linewidth: ~ 0.2 cm^{-1}) and processed using a boxcar averaging system. Figure 4(a) shows the PLE spectra from GaN:Eu,Si codoped thin films with different Si concentrations. Several Eu sites were inferred based on excitation peaks at 585, 588.3, and 591 nm in the ${}^5D_0\text{--}{}^7F_0$ region.^{8,9} In the moderate Si doping range, corresponding to the red emission enhancement region, a satellite peak at 587.5 nm appears next to the 588.3 nm peak. This additional peak could be due to some of the Eu^{3+} ions being in displaced Ga lattice locations. The PLE wavelength difference between the main and satellite peaks is 0.8 nm. This is quite similar to the reported¹⁰ 0.7 nm difference in the PL emission from the ${}^5D_0\text{--}{}^7F_2$ between normal and displaced

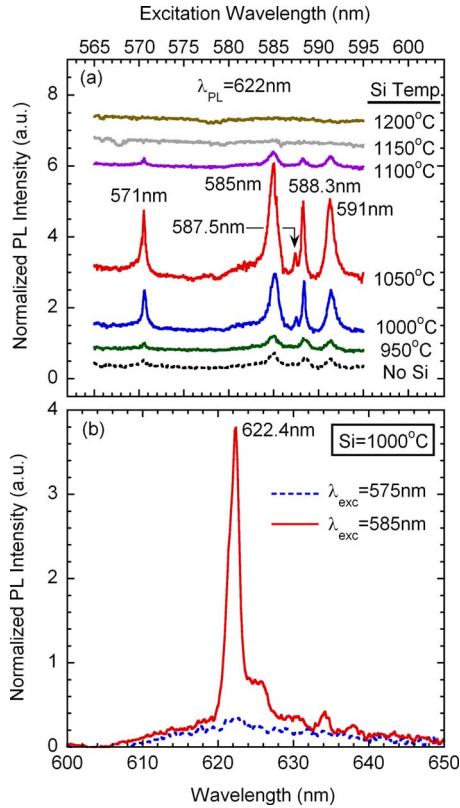


FIG. 4. (Color online) (a) PLE spectra for 5D_0 - 7F_0 region from codoped GaN:Eu,Si thin films. (b) PL spectra excited at 575 nm (nonresonant) and 585 nm (resonant) wavelengths.

Eu sites in GaN thin films. The strong excitation peak at 571 nm is probably an additional line from Eu ions at Ga substitutional sites. As seen from the PLE spectra in Fig. 4(a), Eu^{3+} luminescence under resonant excitation was enhanced by Si codoping, with the maximum enhancement occurring at a Si cell temperature of $\sim 1050^\circ\text{C}$. This trend corresponds very well to the enhancement of Eu^{3+} luminescence excited by above-bandgap pumping. Nonresonant (below bandgap) excitation did not result in any red emission for all samples. This is clearly seen in Fig. 4(b) where a comparison of PL spectra from a codoped GaN:Eu,Si thin film (Si cell temperature of 1000°C) is obtained under resonant excitation (585 nm) and nonresonant excitation (575 nm).

The effect of Si codoping on Eu^{3+} red emission for steady state excitation under small pump power can be explained by the following equation:¹¹

$$I_{\text{PL}} \propto \frac{N_{\text{Eu}}^*}{\tau_{\text{rad}}} = \sigma_{\text{eh}} \phi N_{\text{Eu}} \frac{\tau}{\tau_{\text{rad}}}, \quad (1)$$

where the PL intensity is proportional to the Eu^{3+} ions concentration N_{Eu} , the lifetime τ , the excitation cross section through electron-hole recombination σ_{eh} , the carrier flux ϕ , and inversely dependent on the radiative lifetime τ_{rad} . We can draw some preliminary conclusions regarding to the mecha-

nism responsible for the Eu^{3+} PL intensity dependence on Si concentration by considering the trend shown in the Fig. 3(b) insert. High Si doping levels (0.08 to >0.1 at. %) result in a decrease in PL lifetime (with additional nonradiative decay processes produced by defects surrounding Eu^{3+} ions such as Si-Si complexes and Si related defects). Combined with the simultaneous decrease in Eu concentration (as seen in Fig. 1), this can certainly explain the reduction in PL intensity. It is more difficult to identify the mechanism responsible for PL enhancement. In the enhancement region, the Si doping is at “moderate” levels (0.04–0.07 at. %). The observed increase in PL lifetime could be due to a more highly spaced Eu^{3+} distribution. However, this is not sufficient to explain the sharp increase in PL intensity in this region. Another possible factor is an increase in excitation cross section due to the formation of Eu-Si complex sites. Moreover, the shallow energy levels introduced by moderate Si doping could provide another efficient energy transfer channel, resulting in Eu^{3+} PL emission enhancement.

In summary, the effect of Si codoping on Eu^{3+} photoluminescence of GaN:Eu thin films was investigated. Significant enhancement in Eu^{3+} red luminescence was obtained for a moderate range of Si concentration (0.04–0.07 at. %), while luminescence reduction resulted at high Si concentration (>0.08 at. %). A major role of Si atoms has to do with their effect on the Eu PL lifetime, resulting in an increase in lifetime at low-moderate concentration (possibly by shielding Eu-Eu interactions) followed by a lifetime decrease at higher concentration (due to defect generation). Other possible mechanisms for PL enhancement include an increase in excitation efficiency due to Eu-Si complex formation.

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