Radiation damage mechanisms for luminescence in Eu-doped GaN

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(Received 6 October 2006; accepted 5 January 2007; published online 1 March 2007)

Thin films of Eu-doped GaN were irradiated with 500 keV He+ ions to understand radiation damage mechanisms and to quantify luminescence efficiency. The dependence of ion-beam-induced luminescence intensity on ion flux was consistent with the simultaneous creation of nonradiative defects and the destruction of Eu-based luminescence centers associated with 4f-4f core-level transitions in Eu3+. This model contrasts with a previous description which takes into account only nonradiative defect generation in GaN:Eu. Based on light from a BaF2 scintillator standard, the luminescent energy generation efficiency of GaN:Eu films doped to ~3 x 1018 cm−3 Eu is estimated to be ~0.1%. © 2007 American Institute of Physics. [DOI: 10.1063/1.2696527]

I. INTRODUCTION

Eu-doped GaN is a promising material for optoelectronic devices, having demonstrated efficient conversion of energetic electrons to light.1–11 The triply ionized Eu atom, situated in the Ga position of the GaN lattice, exhibits strong photoluminescence at ~621 nm (~2 eV) due to the 4f-4f core-level transition 5D0 → 7F2. This wavelength is technologically important because it facilitates fabrication of monolithic GaN-based devices composed of diodes emitting light at red, green, and blue wavelengths.12 Further, Eu-doped GaN films show potential for operation in radiation environments, since luminescence remains relatively constant even after exposure to high fluxes of 3 MeV electrons. It is hypothesized that traps introduced in the GaN matrix during irradiation have little effect on the Eu-related luminescence because the distance between nearest neighbor Eu atoms can be made small relative to the minority carrier diffusion length in GaN. Excited electrons are therefore captured by the Eu centers and their energy converted to light before they can nonradiatively recombine with holes in GaN.13

Here we use in situ optical measurements to examine the mechanisms for light emission and damage in Eu-doped GaN thin films. We show that the luminescence due to the Eu ion can be quenched by moderate fluxes of energetic He+ ions, thereby establishing the ultimate limits of radiation tolerance in this material. We quantitatively explain the origin of the damage by introducing a model that takes into account both the creation of nonradiative traps and the destruction of Eu3+ luminescent centers. Finally, we estimate the efficiency of the ion-beam-induced luminescence process by making use of a well-characterized scintillator, BaF2.

II. GaN:EU THIN FILM PREPARATION, ION BEAM DAMAGE, AND CHARACTERIZATION

Undoped GaN(0001) films on sapphire substrates were synthesized by Cree, Inc., and implanted to ~5 x 1014 cm−2 with Eu ions at 190 keV, 5° tilt relative to the wafer normal. Films were ~2.4 μm thick, n type, with electron carrier concentration less than 1016 cm−3. Implanted wafers were diced into 1 cm2 pieces and then annealed with pieces positioned front-to-front in a N2 ambient at 1025 °C for 90 min to activate the Eu atoms. Subsequently, secondary ion mass spectrometry (SIMS) measurements were performed to establish the concentration of active Eu atoms in the film.14 SIMS showed that some N had evaporated during annealing; atomic concentrations were reduced, for example, by factors of ~100 and 3 at the surface and at a depth of 0.4 μm, respectively, relative to the N concentration at depths of 1 μm and greater. The low surface concentration of N suggests that some Ga droplets are present at the surface, in which Eu is not expected to be active. However, a concentration of ~1.5 x 10−3 Eu remained in GaN at a depth of 0.4 μm, tailing off to noise levels below 5 x 10−7 at a depth of 1 μm. Between depths of 0.4 and 1 μm, the average concentration of active Eu atoms was 3 x 10−5.

Activated GaN:Eu films were exposed to 500 keV He+ in the Lawrence Livermore National Laboratory (LLNL) 4 MeV ion beam accelerator. Films were oriented at 45° to the incoming beam during irradiation and masked with a stainless steel shield such that the area exposed was 7.1 x 10−2 cm2. Dose rates on this area were between 6.9 x 109 and 1.4 x 1012 ions s−1 cm−2. During He+ irradiation, light from GaN:Eu was collected in situ by a 5 mm diameter collimating lens mounted 1.8 cm from the sample. The light was then spectroscopically analyzed and recorded with a cooled detector. Photoluminescence (PL) measurements were also performed on the films before and after irradiation using a 325 nm excitation source operating at room temperature. With SRIM 2003, we estimate the range of 500 keV He+...
ions, incident at 45° to the GaN surface normal, to be ~0.9 μm. After exposure to a sufficient fluence of He⁺ ions, photoluminescence is quenched. Figure 1 shows the photoluminescence spectrum of the GaN:Eu obtained with laser excitation (λ=325 nm), before and after irradiation with 500 keV He⁺ to 5.3 × 10¹⁴ cm⁻². For comparison, the spectrum of He⁺-excited GaN:Eu is shown in Fig. 1 for 500 keV He⁺ with a flux of 6.9 × 10⁹ ions s⁻¹ cm⁻². The spectrum generated by He⁺ ions incident on GaN:Eu is very similar to the PL-generated spectrum, indicating that the same 4f–4f core-level transition in Eu³⁺, ⁵D₀→⁷F₂, is responsible for the observed light in both cases. Surface-emitted ion-beam-induced luminescence and photoluminescence are dominated by Eu³⁺ on the Ga sublattice. The relatively large peak widths obtained in measurement of alpha-induced luminescence are due to larger-diameter optical fibers employed to maximize light collection efficiency.

Figure 2 shows the normalized peak (~621 nm) ion-beam-induced luminescence intensity as a function of fluence. Ion dose rates range between 5.5 × 10¹⁰ and 1.4 × 10¹² ions s⁻¹ cm⁻². The peak intensity is associated with the ⁵D₀→⁷F₁ transition in Eu³⁺ and it decreases following exposure to 500 keV He⁺ ions. Note that the luminescence decay rate is not a strong function of the dose rate over this range. Model results are shown also, as will be discussed.

III. ION BEAM DAMAGE AND LUMINESCENCE ANALYSIS

To understand the photoluminescence decay due to damage from 3 MeV electrons, the density of traps was assumed by Nakanishi et al. to be equal to radiation fluence Φ scaled by the trap production rate Kᵣ.

\[ N = KᵣΦ. \tag{1} \]

This assumption proves successful for these electron irradiation experiments. The trap production rate was calculated to be ~7 cm⁻¹, with a constant radiative recombination lifetime τᵣ of 1 ns a thermal velocity νₜh of 10⁷ cm/s, and capture cross section for nonradiative traps σ of 10⁻¹⁵ cm⁻² (0.1 nm⁻²). For ion-beam-induced luminescence, we assume that the previous analysis developed for photoluminescence remains valid. This is supported by the fact that the emission spectra for the two processes are similar, as shown in Fig. 1. However, we find that the observed decay of luminescence as a function of ion fluence cannot be accounted for by trap production alone. For example, assuming constant τᵣ, the best fit to He⁺ luminescence data is shown as a dashed line in Fig. 2. Significant differences between the measured and modeled data are evident at both low and high fluences.

To explain the observed differences between measured and modeled data for ion-beam-induced luminescence, we first assume that the lifetime for radiative recombination τᵣ can be described with

\[ τᵣ = \frac{1}{σνₜhNᵣ}, \tag{2} \]

where \( Nᵣ \) is the number of radiative recombination centers per unit volume (cm⁻³), σ is the capture cross section, and νₜh is the thermal velocity of carriers. These centers are destroyed by the ion fluence Φ at a rate which is proportional to the number of remaining centers.
\[ \frac{dN_r}{d\Phi} \propto -N_r, \]  

such that the number of radiative centers as a function of fluence is given by

\[ N_r = N_r^0 e^{-\alpha \Phi}, \]

where \( \alpha \) is the cross section for the destruction of radiative centers and \( N_r^0 \) is the initial concentration of radiative centers.

Physically, the mechanism responsible for this observed destruction of luminescent centers is the displacement of \( \text{Eu}^{3+} \) ions from its equilibrium position on the Ga sublattice to an interstitial or antisite position.\(^4\)\(^{16}\) Alternately, a Ga or N atom could be moved by \( \text{He}^+ \) to an interstitial site near the \( \text{Eu}^{3+} \) and thus its quench luminescence. As implanted, the Eu-doped GaN does not exhibit photoluminescence, and relatively high temperatures (>800 °C) are needed to move the Eu atoms into the triply ionized position on the Ga site.\(^17\)

The most important difference between the electron irradiation reported previously and the \( \text{He}^+ \) irradiation described here is that \( \text{He}^+ \) causes \( \sim 100 \times 10^6 \) more nonionizing damage through events such as vacancy creation.\(^18\)

To calculate the rate at which the radiative centers are being destroyed, we assume that the initial concentration of radiative centers is equal to the concentration of active Eu at depths between 0.4 and 1 μm in the GaN:Eu which is \( 3 \times 10^{-5} \) or \( 2.6 \times 10^{18} \) cm\(^{-3} \). With this model, we find that the trap production rate for 500 keV \( \text{He}^+ \) ions is \( \sim 5000 \) cm\(^{-1} \) and that the cross section for radiative center destruction is \( 5 \times 10^{-15} \) cm\(^{-2} \) (0.5 nm\(^{-2} \)). The best fit of the model to the data is shown in Fig. 2. Comparing statistically the old model to the model used in this experiment with an F test, we calculate a less than 0.01% chance that the old model is a better fit for the data. Note that neither model fits well to the data at low fluences, indicating that the rate of nonradiative defect generation may not be constant in this range, as assumed in Eq. (1). To estimate the absolute light emission efficiency of the GaN:Eu scintillator, we use \( \text{BaF}_2 \), an established scintillator with known alpha-to-photon conversion of 720 photons/MeV.\(^19\) With SRM 2003,\(^15\) we calculate the energy deposition in the GaN:Eu as a function of depth. Estimating the active Eu content at \( 3 \times 10^{-5} \) from the measured SIMS profile and assuming comparable surface emission for GaN:Eu and \( \text{BaF}_2 \), we find that the conversion efficiency is \( \sim 0.1\% \).

**IV. CONCLUSION**

In summary, evidence has been found for ion-induced radiation damage in luminescent GaN:Eu thin films that is associated with both the creation of defects and the destruction of luminescent centers. Luminescent centers are destroyed by \( \text{He}^+ \) ions that remove the \( \text{Eu}^{3+} \) from its equilibrium position on the Ga sublattice, or by creation of interstitials near the \( \text{Eu}^{3+} \) ion. For 500 keV \( \text{He}^+ \) ions, the trap production rate is \( \sim 5000 \) cm\(^{-1} \) and the cross section for radiative center destruction is \( 5 \times 10^{-15} \) cm\(^{-2} \) (0.5 nm\(^{-2} \)). We estimate that lightly Eu-doped (2.6 × 10\(^{18} \) cm\(^{-3} \)) GaN films convert radiative energy to light with \( \sim 0.1\% \) efficiency. Although this efficiency is modest, it is encouraging since the films were not optimized for luminescence. Now that the role of radiation-induced displacement damage has been quantitatively demonstrated, together with the ultimate radiation tolerance of this material, annealing and other strategies for defect modification can be more effectively pursued.

**ACKNOWLEDGMENTS**

This work was performed under the auspices of the U.S. Department of Energy by the University of California Lawrence Livermore National Laboratory under Contract No. W-7405-ENG-48. The authors thank Professor A. Steckl (University of Cincinnati) and Dr. S. O. Kucheyev (LLNL) for useful discussions, and Dr. A. Pertica and T. Graff (LLNL) for assistance with luminescence measurements and sample preparation, respectively.

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\(^14\)SIMS analysis was performed by Evans Analytical Group.


