

PL characterization of GaN scintillator for radioluminescence-based dosimetry

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ABSTRACT

Via photoluminescence (PL) measurements, we have investigated GaN (which is a widely employed material in optoelectronics) to be used as scintillator for developing implantable dosimetric probes. The studied Si-doped n-type GaN samples have common dominant band-edge emission at room temperature, with a strong doping-dependence on their PL spectra. Si-doped GaN with 10^{18} cm^{-3} concentration exhibits a non-negligible yellow luminescence (YL) or red luminescence broad band contribution, which is probably due to Ga vacancy native defect. However, heavily-doped GaN ($\sim 1.5 \times 10^{19} \text{ cm}^{-3}$) has much more intense band-edge emission, with no significant contributions of lower-energy bands. The dominant band-edge emission peak remains unchanged at 3.4 eV for both concentrations, and may be accounted for by considering combined effects of band-gap narrowing and Fermi level rising. It has also been demonstrated by back-side PL collection that, due to bulk self-absorption, the dominant peak is shifted to 3.25 eV DAP (donor-acceptor-pair) or e-A (conduction-band-to-acceptor) band. At low temperatures (up to 200 K), PL intensity of heavily-doped GaN is dominated by a DBE (donor-bound exciton) line (D^0X_A at 3.467 eV for $T = 10 \text{ K}$). When further increasing the temperature, band-to-band recombination becomes dominant with red-shift of the emission peak in connection with gap narrowing. The shift in peak wavelength from 10 K to room temperature is about 5 nm, while the corresponding PL integrated intensity is decreased only by 30%. Irradiating samples at room temperature to a 200 Gy dose with 6 MeV photon and electron beams causes a slight increase on defect-related DAP or e-A line and YL broad band, but the effect is not noticeable for heavily-doped GaN.

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1. Introduction

GaN has increasingly been used as a wide direct-gap semiconductor for fabricating short-wavelength optoelectronics devices. On the other hand, it can also be employed as a scintillator material. It has high light yields ($\sim 10^5$ Photons/MeV) and very short rising and decay times ($< 1 \text{ ns}$ for its near-band-edge transitions). Its near-band-edge emission in UV range is convenient for using sensitive photodetectors such as photo-multiplier tube (PMT) and avalanche photodiode (APD) in instrumental developments. Its narrow-band UV emission enables background rejection by simple spectral filtering.

The luminescent characteristics of GaN are of primary importance for its scintillation use. For developing an implantable GaN-based dosimetric probe, we have investigated the luminescent properties of this material by photoluminescence (PL) spectral measurements. By considering that PL spectral characteristics are similar to radioluminescence (RL) ones, we have carried out PL characterization of GaN to observe effects of parameters, such as doping concentration and temperature.

However, it should be mentioned that even if both UV excitation and high-energy irradiation produce free carriers resulting in radiative recombination (luminescence emission), the distribution of the generated free carriers is not the same between these two cases. For a given small-size crystal sample (e.g. $\sim 1 \text{ mm}^3$), an UV excitation beam of 5.08 eV has an absorption depth of only a few ten nanometers [1], while high-energy rays may pass through the sample without significant energy loss. Thus, PL signal is mainly contributed from a shallow layer and is more affected by surface effects, while RL has more bulk contribution because of

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fairly uniform distribution of excited free carriers [2]. It can therefore be expected that, due to bulk self-absorption effect [3] that reshape the near-band-edge PL emission peak, the RL emission peak is red-shifted compared to the PL one. To assess this effect, we have also measured PL spectra via back-side signal collection.

There have been extensive studies on doping effects via PL measurements. High-quality undoped GaN has indicative strong near-band-edge emission, but a typical spectrum also exhibits a lower-energy broad band contribution often called yellow luminescence (YL) or red luminescence band resulting from deep-level transitions. This YL broad band is defect-related, and probably due to Ga vacancy native defect [4]. It is not well controlled, and may cause uncertainty and unreliability for the scintillator to perform radioluminescence (RL) conversion. This undesirable contribution can, however, be minimized by introducing a high doping level in the material. It has been reported that heavily Si-doped n-type GaN suppresses YL band contribution, with plausible explanation that a sufficient Si-donor concentration reduces effectively Ga vacancies [5]. For our dosimetric application, heavily-doped GaN is preferred. We have thus worked on samples with two concentrations: 10^{18} cm^{-3} and $1.5 \times 10^{19} \text{ cm}^{-3}$ respectively.

When exploiting near-band-edge emission as useful light output, it is needed to evaluate variations of signal intensity and peak position depending on temperature. This involves identification of dominant near-band-edge emission mechanisms. Predictably, at low temperatures carriers in GaN combine to form free or impurity-bound excitons, and at room temperature (RT) a thermal equilibrium of free excitons and separate electrons and holes would be expected [6]. Nevertheless, we need to verify this prediction, especially for heavily-doped GaN, in which case the temperature dependence is expected to be very different from undoped one because of doping effects on band-to-band recombination and excitonic formation.

We have also performed PL measurements on samples irradiated by photon and electron beams to estimate irradiation effects.

2. Experiment

2.1. Materials

Si-doped n-type GaN substrates were provided by LUMILOG¹, France. They are strain-free bulk GaN grown by hydride-vapor-phase-epitaxy (HVPE) [7]. The activation energy of Si_{Ga} shallow donor is 30 meV [8]. However, silicon may also appear as a shallow acceptor in GaN by substituting an N atom [9], and the binding energy of Si_N acceptor is 224 meV according to [10], although the formation of Si_N is less probable than Si_{Ga}.

We used two wafers of 0.3mm and 1.4 mm thickness respectively, having different concentrations: 10^{18} cm^{-3} and $1.5 \times 10^{19} \text{ cm}^{-3}$. The samples are denoted as A-sub and B-sub ones respectively.

2.2. PL experimental set-up

The PL characterization of GaN was carried out using a modified measuring system initially developed for SiC studies. The UV excitation was a 244 nm (5.08 eV) doubled-frequency argon laser beam. The PL spectral measurement was performed using a grating monochromator (Jobin-Yvon HR 640) equipped with a GaAs photomultiplier tube (PMT) (HAMAMATSU 5701). Synchronous detection technique was implemented by chopping the laser beam at a modulation frequency of about 110 Hz, and by employing a lock-in amplifier (EG&G 5209) connected to the PMT electrical out-

put. The lock-in amplifier was followed by a signal-acquisition chain and a PC for data monitoring and processing. A number of optical components (long pass filters, mirrors and lens) were inserted in UV excitation and PL collection paths. The focused excitation light spot was about 300 μm in diameter. For low temperature measurements, the sample was fixed in a helium cooled cryostat. The experimental set-up for front-side and back-side collection is illustrated in Fig. 1a and b respectively.

PL measurements were made with setting of the following parameters. Focused excitation power density: $\sim 10^{-2}$ or 10 W cm^{-2} ; time constant of the lock-in amplifier's low-pass filter: $\tau = 300 \text{ ms}$; monochromator's spectral scanning range: 300 to 800 nm (using successively 285 nm and 600 nm long pass filters for excitation rejection and to prevent signal aliasing); spectral resolution: 0.1–2.5 nm. All spectra were corrected from the apparatus response.

3. Results and discussion

3.1. Doping effects

Fig. 2 shows room temperature front-side PL spectra of the A-sub (10^{18} cm^{-3}) and B-sub ($1.5 \times 10^{19} \text{ cm}^{-3}$) samples with an excitation power density of 10 W cm^{-2} .

Both samples exhibit a dominant emission peak at $E_p = 3.40 \text{ eV}$, which is attributed to band-to-band emission. It is noted that at room temperature, band-to-band transition in high-quality GaN has preponderant emission over excitonic transitions [11].

We have verified the peak position with 1% of the initial UV excitation power density, and have seen it unchanged. Both samples having the same peak position may look surprising if we consider band-gap narrowing due to heavy doping. This effect predicts a low-energy shift for a higher doping concentration. However, we may also need to consider another effect: the Fermi level in the conduction band of the heavily-doped semiconductor increases with doping concentration. As more electrons near the Fermi level contribute to band-to-band transition, the resulting emission may be enhanced with slight high-energy shift. Therefore, we may consider both combined effects to account for the observed peak position.

The A-sub sample displays a much lower near-band-edge emission peak than that of the B-sub one. This is predictable because band-to-band transition is directly related to doping concentration. Although the band-to-band contribution remains dominant, the A-sub spectrum shows a visible DAP (donor-acceptor-pair) or e-A (conduction-band-to-acceptor) band at 3.28 eV and a broad YL (yellow luminescence) or RL (red luminescence) band extending to near IR (infra red). In contrast, the B-sub sample exhibits a single intense peak. It may partly be explained by the predominance of band-to-band emission that may mask other contributions. Other explanations may include Ga vacancy replacement by Si dopant [5]. The PL integrated intensity ratio of the YL band to the near-band-edge peak is 50% for the A-sub sample and 3.7% for the B-sub one respectively.

Fig. 3 shows room temperature back-side PL spectra of the two samples, compared with the front-side ones.

Due to bulk self-absorption filtering [3], the emission peak is shifted to 3.28 eV and 3.25 eV for the A-sub and B-sub samples respectively. The peak corresponds to DAP or e-A band. It means that this effect becomes negligible for emitted photons at such energy. We may thus consider the situation of radioluminescence (RL) having both shallow and deep bulk contributions, and roughly estimate that the dominant RL peak of the heavily-doped GaN will be located between 3.25 eV and 3.40 eV at room temperature.

¹ <http://www.lumilog.com>.

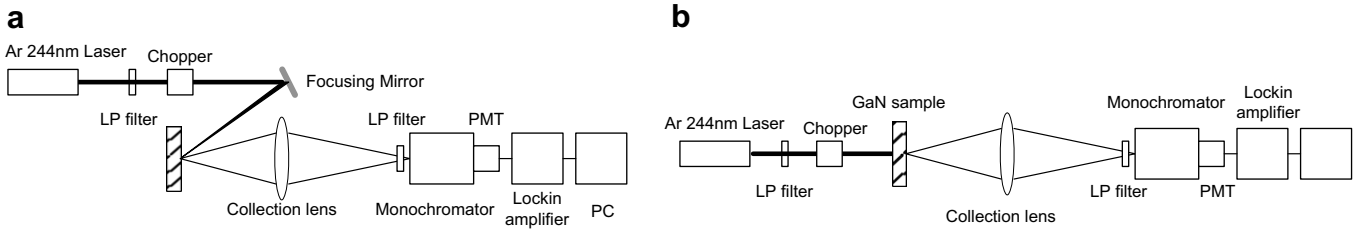


Fig. 1. (a) Front-side and (b) back-side PL measurement set-up.

3.2. Temperature dependence

It may be worth recalling that the semiconductor has a wider band-gap at a lower temperature, and that free or bound exciton emission may become predominant. Fig. 4 shows PL spectra of the heavily Si-doped GaN corresponding to different temperatures. At 10 K the peak at 3.467 eV is assigned to neutral-donor-bound exciton transitions (D^0X_A). From 10 to 200 K, the peak position remains practically unchanged. This may suggest increasing contribution of free exciton emission when rising temperature, because excitons trapped by donors delocalize, resulting in quenching of D^0X lines in favor of the free exciton emission. This suggestion is supported by reported results [12,13] which showed domination

of FX_A and D^0X_A lines at low temperatures, with much slower thermal quenching of the former than the latter. When further increasing the temperature, band-to-band recombination becomes dominant with red-shift in connection with gap narrowing. The shift in peak wavelength in this 10 K-room temperature range is about 5 nm (47 meV), with bandwidth enlarging from 1.5 nm (14 meV) to 8.5 nm (80 meV). The corresponding PL integrated intensity is decreased only by 30%. This moderate intensity variation with remaining high level of luminescence for $T > 200$ K is due to heavy doping allowing enhanced emission.

3.3. Effects of photon and electron irradiations

To evaluate effects of photon and electron irradiations on the luminescence properties of the chosen doped GaN scintillator,

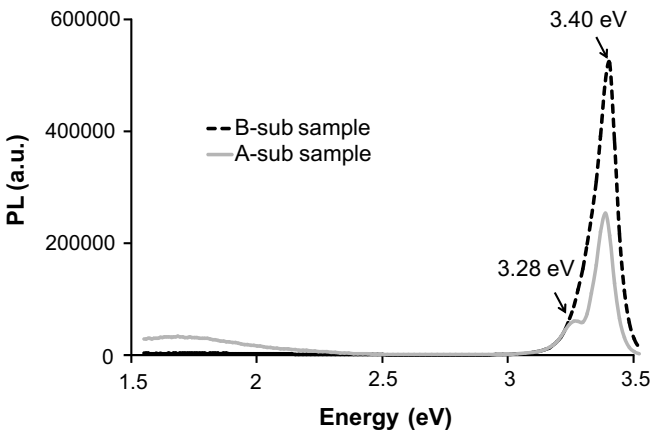


Fig. 2. Room temperature front-side PL spectra of the A-sub (10^{18} cm^{-3}) and B-sub ($1.5 \times 10^{19} \text{ cm}^{-3}$) samples.

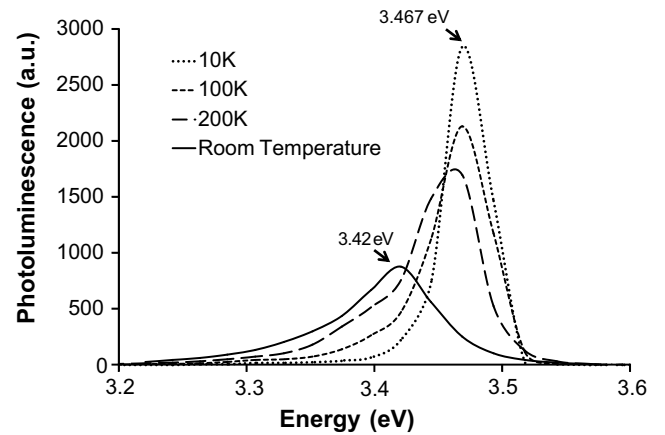


Fig. 4. PL spectra of the B-sub sample at different temperatures.

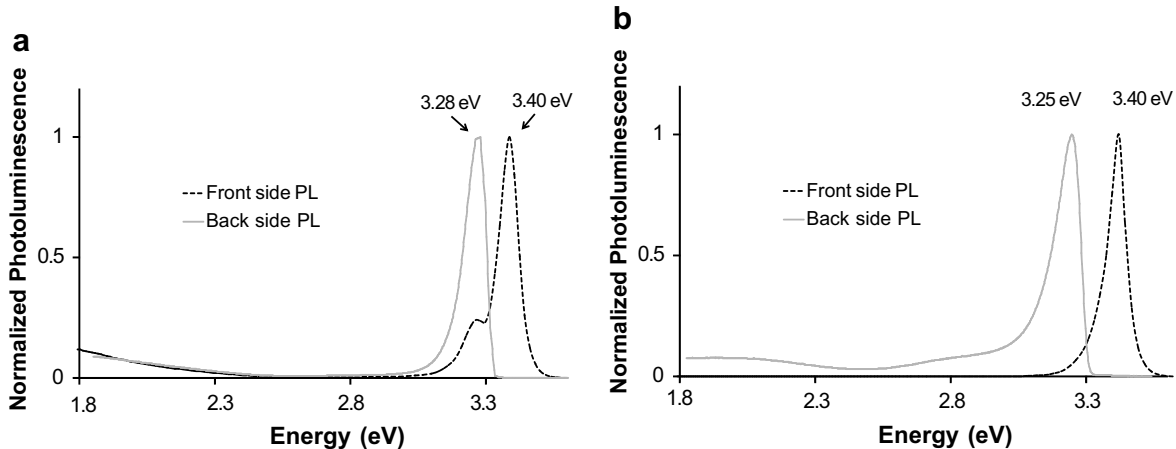


Fig. 3. Room temperature back-side PL spectra compared with the front-side ones (a) for A-sub and (b) B-sub samples.

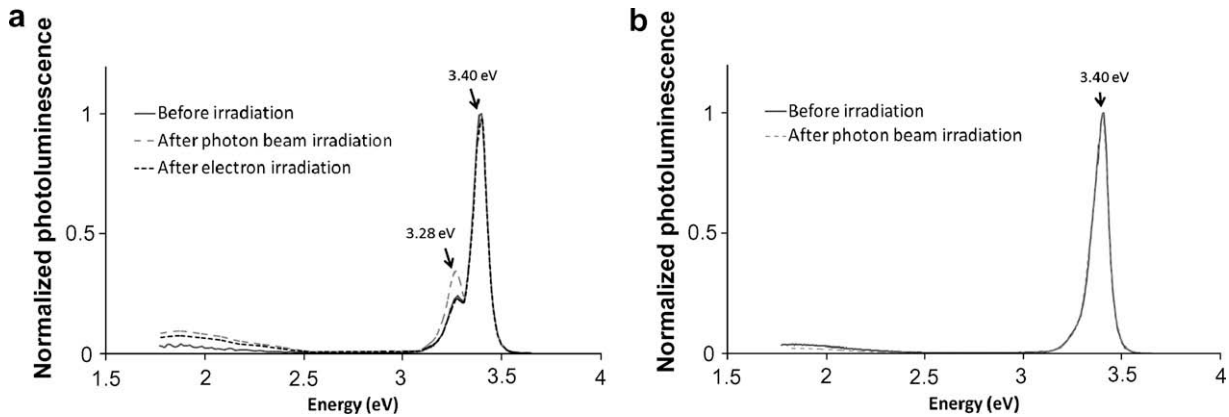


Fig. 5. PL spectra for 200 Gy irradiated (a) A-sub and (b) B-sub samples.



Fig. 6. Radioluminescence emission of A-sub sample during 6 MeV photon beam irradiation.

some A-sub and B-sub samples were irradiated by 6 MeV photon (bremsstrahlung photons) or electron beams from a radiotherapy linear accelerator (Elekta SLi). Each sample received a 200 Gy dose. The irradiated samples were measured and the obtained PL spectra were compared with those of non-irradiated ones (shown in Fig. 5).

At room temperature, non-irradiated and irradiated samples have their PL spectra practically superimposed. It has been reported that electron irradiation may create Ga vacancies and thus increasing YL intensity [14,15]. However, in our experimental conditions, although a small YL increase is observed for A-sub samples, YL contribution remains negligible in the irradiated heavily-doped samples. Most importantly, the measured results show no observable irradiation effects on the PL intensity peak. This assures us of no irradiation-induced degradation for the radioluminescence conversion characteristic of the GaN transducer.

With the aim of developing implantable dosimetry by using Si-doped GaN as scintillator material, we verified if it has high radioluminescence output by taking a picture of the A-sub sample under radiotherapy irradiation with a cooled CCD camera (LEICA, DFC340-FX) (see Fig. 6). This irradiation employed a 6 MeV photon beam and was performed according to a standard therapeutic procedure (a dose rate of 300 monitor units per minute applied for 10 s). Despite poor UV sensitivity of the camera, the image shows clearly the luminescent sample.

4. Conclusion

By PL spectral characterization, we have investigated GaN, not for optoelectronics applications, but for scintillation in implantable

dosimetry. Si-doped n-type GaN substrates at room temperature have PL spectra exhibiting dominant band-edge emission, with a strong doping-dependence on their YL broad band. Indeed, its contribution is still significant for a concentration of 10^{18} cm^{-3} , while heavily-doped GaN with $1.5 \times 10^{19} \text{ cm}^{-3}$ has enhanced PL intensity with an integrated intensity ratio of YL band-to-band-edge peak lower than 4%. The dominant band-edge emission peak remains unchanged at 3.4 eV for both concentrations, but can be red-shifted in the case of radioluminescence, due to bulk self-absorption effect. At low temperatures (up to 200 K), PL intensity of heavily-doped GaN is mainly contributed by bound and free excitons. Irradiating heavily-doped GaN to a 200 Gy dose with 6 MeV photon and electron beams does not induce noticeable PL variations.

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