

Nonradiative Recombination Processes in GaN-based Semiconductors Probed by the Transient Grating Method

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Transient grating (TG) method with nanosecond pulsed laser was used to detect the heat released by the nonradiative recombination of carriers and/or excitons in GaN-based semiconductors at room temperature. Obtained TG signal rises immediately within the excitation pulse (few nanosecond) and decayed within few tens nanosecond. This decay profile can be fitted by a single exponential function. By solving the diffusion equation, it was found that the pre-exponential factor and the rate constant obtained from fitting suggest the increase of temperature (ΔT) originating from the nonradiative recombination and the thermal diffusivity (D_{th}) in material, respectively. Obtained D_{th} value ($0.41 \text{ cm}^2\text{s}^{-1}$) is close to the theoretical value ($0.44 \text{ cm}^2\text{s}^{-1}$) calculated by the density (ρ), heat capacity (C_p), and thermal conductivity (λ_c) as $D_{th}=\lambda_c/\rho C_p$. The excitation power dependence of ΔT showed the linear relationship, which is different from the reported case of ZnSe. Such discrepancy can be understood as a difference in capture cross section of carriers and/or excitons to nonradiative recombination centers.

KEYWORD: nonradiative recombination, transient grating, GaN-based semiconductor, thermal diffusivity

1. Introduction

GaN-based semiconductors are very advantageous materials for light emitting diode (LED) and laser diode (LD) within blue-UV spectral region. In spite of high threading dislocation density (10^8 - 10^{10} cm^{-2}), the external quantum (η_{ext}) of emission for GaN-based LEDs are very high (10-15%) which is comparable to the value achieved in ZnSe-based semiconductors with low etch pit densities ($<10^4 \text{ cm}^{-2}$). Some group studied the relationship between the threading dislocation and the emission efficiencies probed by the cathodoluminescence (CL) mapping, or site selective time-resolved photoluminescence (PL) and so on.¹⁻³ Obtained results show that macroscopic dislocation do act as nonradiative recombination centers. It is likely that point defects such as vacancy, anti-site, or complex centers coupled with impurities are the factor to limit the emission efficiency.¹⁻³ Such measurements are based on the observation of radiative recombination processes of carriers and/or excitons in materials. On the other hand, direct observations of nonradiative recombination dynamics have been only few reports so far.⁴ However, both

radiative and nonradiative processes should be known to elucidate the carrier dynamics and to develop the device properties because the internal quantum efficiency (η_{int}) is determined from the radiative and nonradiative recombination lifetime.

The heat dynamics can be assessed by measuring the photo-induced refractive index change (Δn) by using the Transient grating (TG) method.⁵ The TG method is one of the third order nonlinear spectroscopy, which has been used to detect the several optical properties of semiconductor at the very fast region with the pico or femto second order.⁴ However, the observation of heat dynamics in semiconductors by the TG method with a nanosecond pulsed laser has not so far been investigated. Quite recently, we reported that the thermal dynamics of nonradiative recombination processes in ZnSe-based semiconductors can be detected directly by using the TG method.⁶ In this paper, we observed the nonradiative recombination processes of GaN-based semiconductors directly by the TG method with a nanosecond pulsed laser. Obtained results were compared to there in ZnSe-based semiconductors.

2. Experimental procedure

The sample of GaN epitaxial layer was grown on a (0001) oriented sapphire substrate with a thickness of 4 μm by a two-flow metalorganic chemical vapor

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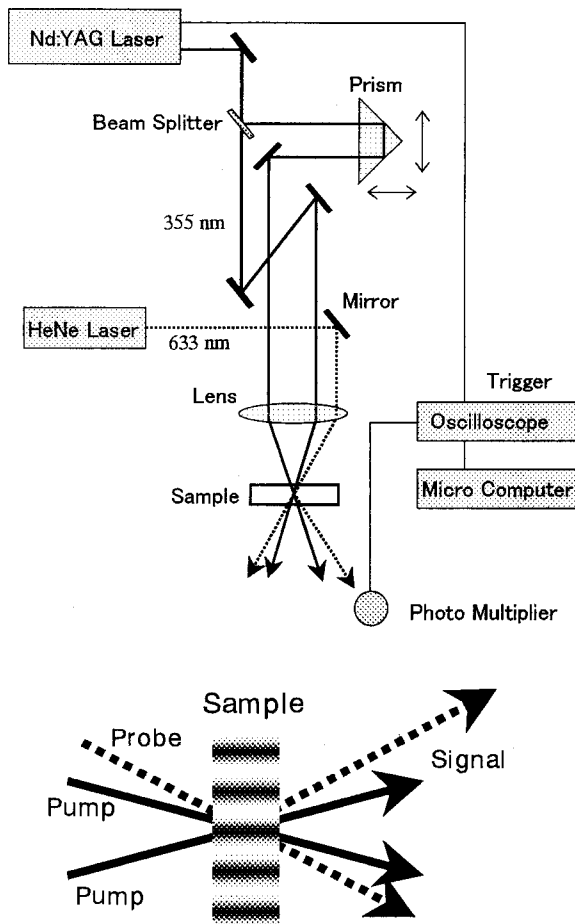


Fig. 1 Experimental setup (up) and configuration of the excitation and probe beams (down) of the transient grating method with a nanosecond pulse laser.

deposition (MOCVD). The detail growth condition has been reported elsewhere⁷ For comparison, we used 0.9 μm -ZnSe homoepitaxial layer grown on ZnSe substrate by molecular beam epitaxy (MBE).⁸

The experimental set up, configuration of the excitation and probe beams of the TG method are shown in Fig. 1. The frequency tripled beam of Nd:YAG laser (Spectra Physics DC-11; $\lambda_e=355\text{nm}$) was used for excitation. The interference pattern is created by crossing two excitation beams with an angle θ in the sample materials. The fringe spacing Λ is given by

$$\Lambda = \lambda_e / 2\sin(\theta / 2). \tag{1}$$

Then, the light intensity in the crossing region is moderated as follows (Optical grating).

$$I(x) = I/2 (1 + \cos qx). \tag{2}$$

Where q is the grating vector given by

$$q = 2\pi/\Lambda. \tag{3}$$

The sample is excited by this optical grating and the carriers and/or excitons are created. Then, the densities of carriers and/or excitons are also moderated along the optical grating (population grating). The excited area releases the heat by the nonradiative recombination of carriers and/or excitons and the temperature of the sample is modulated (thermal grating). The refractive index (n) and the absorbance (k) of the materials are also modulated by these grating. Such modulation of optical properties ($\Delta n, \Delta k$) are similar to the refractive grating. A probe beam from a He-Ne laser (633nm) was partly diffracted (TG signal) by these gratings. The intensity of the TG signal can be written by

$$I_{TG} = \alpha \Delta n^2 + \beta \Delta k^2 \tag{4}$$

where α and β are constants. The TG signal was detected by a photomultiplier tube (Hamamatsu R-928) after isolation from the probe light with a pinhole and a glass filter (Toshiba R-62), recorded with a digital oscilloscope (Tektronix 2430A), and analyzed with a microcomputer. The signals were averaged about 320 times to improve the S/N ratio. The whole measurements have been done at room temperature (23°C).

3. Result and discussion

Figure 2 shows the time profile of a typical TG signal taken for GaN and ZnSe epitaxial layers. The crossing angle of two excitation beams and fringe

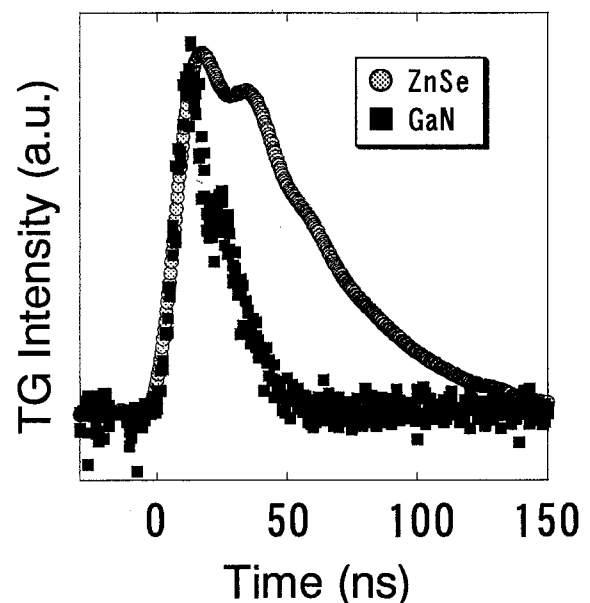


Fig. 2 Time profile of the TG signal of \circ ZnSe and \blacksquare GaN epitaxial layer at room temperature.

space are 4° and $4.7\mu\text{m}$, respectively. These signals rise immediately within the excitation pulse (few nanosecond) and decay within few tens nanosecond. This signal is due to the population grating and/or thermal grating. When the two components contribute simultaneously to the TG signal, the analysis of the TG signals should be very difficult. However, with few tens nanosecond region after excitation, the excitons or carriers should be already terminated. Therefore, the obtained TG signal should be due to only the thermal grating.

To analyze the time profile of the TG signals, the time profile of the carrier dynamics should be considered. The time and spacial dependence of the carrier density $N(x, t)$ is given by the following rate equation.

$$\frac{dN(x, t)}{dt} = D \frac{\partial^2 N(x, t)}{\partial t^2} - (k_{\text{rad}} + k_{\text{non}})N(x, t) \quad (5)$$

where k_{rad} and k_{non} are the radiative and nonradiative recombination rate constants (inverse of the lifetime) and D is the diffusion coefficient of carriers and/or excitons. Then, the temperature change $\delta T(x, t)$ by the nonradiative recombination of the carriers are given by

$$\frac{d\delta T(x, t)}{dt} = ak_{\text{non}}\delta T(x, t) + D_{\text{th}} \frac{\partial^2 \delta T(x, t)}{\partial t^2} \quad (6)$$

where, D_{th} is thermal diffusivity in the materials and a is the proportional constant. By solving Eq. (5)-(6) with condition $D \gg D_{\text{th}}$, following relationship is obtained.

$$\delta T(q, t) = \frac{ak_{\text{non}}N(q, 0)}{k_{\text{rad}} + k_{\text{non}} + Dq^2} \left\{ \exp[-(k_{\text{rad}} + k_{\text{non}} + Dq^2)t] + \exp(-D_{\text{th}}q^2t) \right\} \quad (7)$$

where $\delta T(q, t)$ is the Fourier component of $\delta T(x, t)$. Because the diffusion processes of carriers are slower than the recombination processes ($k_{\text{rad}} + k_{\text{non}} \gg Dq^2$) and faster than the thermal conduction ($D \gg D_{\text{th}}$), Eq. (7) can be reduced as follows.

$$\delta T(q, t) = \frac{ak_{\text{non}}N(q, 0)}{k_{\text{rad}} + k_{\text{non}}} \exp(-D_{\text{th}}q^2t) \quad (8)$$

By Eq. (4), the TG signal intensity is given by the

sum of the square of Δn and Δk . As ZnSe and GaN-based semiconductors do not have the absorption at the wavelength of the probe beam (633nm), the TG signal is contributed only from Δn . The time and spacial dependence of the the refractive index change by the temperature change is given by

$$\delta n(q, t) = \frac{dn}{dT} \delta T(q, t). \quad (9)$$

Therefore, the time profile of the TG signals can be explained by following equation.

$$I_{\text{TG}}(t)^{1/2} \propto \Delta T \exp(-D_{\text{th}}q^2t) \quad (10)$$

where ΔT is the temperature change from the heat released by the nonradiative recombination processes of carriers and/or excitons. This equation indicates that the decay profile of the TG signals should be fitted by a single exponential function. Therefore, from the pre-exponential factor and the decay rate constant, we can obtain ΔT by the nonradiative recombination and D_{th} . D_{th} is obtained as $0.084 \text{ cm}^2\text{s}^{-1}$ and $0.41 \text{ cm}^2\text{s}^{-1}$ for ZnSe and GaN, respectively. D_{th} of GaN is about 5 times larger than that of ZnSe, indicating that GaN has a merit for driving the heat out of an active layer. D_{th} can be calculated theoretically by $D_{\text{th}} = \lambda_c / \rho C_p$. By using the literature values ($\lambda_c = 0.19 \text{ Wcm}^{-1}\text{K}^{-1}$, $\rho = 5.266 \text{ gcm}^{-3}$, and $C_p = 0.0086 \text{ calg}^{-1}\text{K}^{-1}$ as ZnSe, $\lambda_c = 1.3 \text{ Wcm}^{-1}\text{K}^{-1}$, $\rho = 6.095 \text{ gcm}^{-3}$, and $C_p = 9.745 \text{ calmol}^{-1}\text{K}^{-1}$ as GaN), D_{th} was calculated as $D_{\text{th}} = 1.00 \text{ cm}^2\text{s}^{-1}$ and $0.44 \text{ cm}^2\text{s}^{-1}$

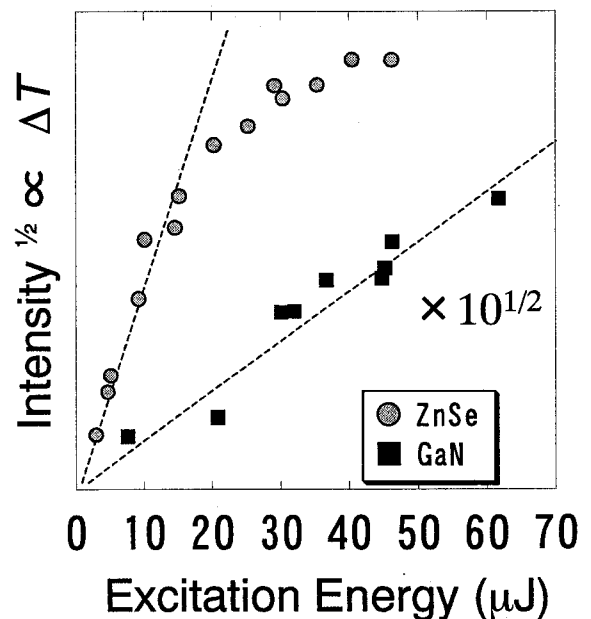


Fig. 3 Excitation energy dependence of the root square of the TG signal of \bullet ZnSe and \blacksquare GaN

for ZnSe and GaN, respectively. These values are close to the experimental one.

Recently, we reported the excitation power dependence of ΔT of ZnSe and ZnCdSe/ZnSe quantum well and found that the ΔT in ZnSe was saturated under the high excitation energy region.⁶ This phenomenon probably suggests that photo-generated carries or excitons in ZnSe-based semiconductors are more easily trapped by the nonradiative recombination centers, resulting in the lower threshold carrier density for the saturation. The radiative processes of ZnSe and GaN are similar (the external quantum efficiencies of LEDs of both materials are 10-15%), but the nonradiative processes of both materials may be different. Therefore, to elucidate the more detail information on the nonradiative recombination, we measured the excitation energy dependence of the TG signals of GaN and compared with that of ZnSe.

Fig. 3 show the excitation power dependence of GaN and ZnSe. The straight lines are guide for eyes. It was found that the nonradiative center in GaN was not saturated, which is different from the reported case of ZnSe. Such discrepancy can be understood as a difference in the nonradiative recombination dynamics of the carries and/or excitons. This is probably related to the fact that GaN epitaxial layers show substantially high PL efficiency in spite of the high dislocation in the crystals. In many semiconductors including ZnSe, dislocations of the crystals act as a nonradiative centers. However, recently, we reported that the nonradiative recombination lifetime of GaN is not so sensitive to the dislocation densities by using the time and spatially resolved PL spectroscopy.⁹ As mentioned in the section of introduction, the limiting factor is not probably macroscopic defects but point defects. Such difference in the nature of the nonradiative centers may reflect the variance of excitation energy dependence of ΔT between GaN and ZnSe. We considered that the carriers in GaN-based are hardly trapped in the nonradiative recombination centers. This property should be due to the immobility of carriers and to low diffusivities of the carriers in GaN-based semiconductor. This fact should be the origin of the strong emission intensity in GaN-based semiconductor despite the large dislocation densities. Similar measurement of InGaN/GaN is in progress and would give valuable information on the optical properties.

4. Conclusion

It was found that the TG method is the powerful tool to detect the thermal dynamics of nonradiative recombination processes of carries and/or excitons in GaN-based semiconductors. Thermal diffusivity in GaN obtained by the decay rate constant of the TG signals ($D_{th} = 0.41 \text{ cm}^2\text{s}^{-1}$) was close to the calculated one ($D_{th} = 0.44 \text{ cm}^2\text{s}^{-1}$). We found that the nonradiative dynamics of GaN is different from that of ZnSe. It is possible to obtain further detailed information on recombination process by the quantitative estimation of the nonradiative processes probed by the TG method and the radiative processes probed by the PL spectroscopy. It is important to note that detailed information on the optical properties such as the ratio between internal quantum efficiency and external one by comparing nonradiative and radiative processes. Such an approach is in progress.

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