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Photothermal processes of wide-bandgap semiconductors probed by the transient grating method

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Transient grating method was used to detect the nonradiative recombination of carriers in the wide-bandgap semiconductors such as ZnSe homoepitaxial layer, ZnCdSe/ZnSe single quantum well (SQW), and GaN epitaxial layer. The time profile of the TG signals can be fitted by the exponential function and the thermal diffusivities of the samples were obtained from the decay rate constants. The temperature change (ΔT) due to the nonradiative processes was also obtained by the signal intensities. A remarkable difference in excitation power dependence on ΔT between ZnSe and GaN was observed. This phenomenon can be understood as a difference of the nonradiative recombination dynamics of the photo-generated carriers and/or excitons.

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ZnSe and GaN-based wide-bandegap semiconductors are very advantageous materials for light emitting diode (LED) and laser diode (LD). Optical properties and functions of semiconductor materials are controlled by the recombination dynamics of carriers and/or excitons created by photo excitation or electron injection. To develop the device properties, the carrier dynamics of wide-bandegap semiconductors have been studied by several spectroscopic method based on the observation of radiative recombination processes by measuring the photoluminescence (PL), electricluminescence (EL), or cathodoluminescence (CL). 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 are very difficult and there have been only few reports until now. However, the nonradiative processes are very important for the optical prosperities of materials, because the internal quantum efficiency of emission is decided from the ratio between radiative and nonradiative recombination processes. Moreover, it was found that the heat released by the nonradiative processes reduce the device lifetime.

Since the heat is released and then diffused by the generation of phonon in this process, it should be possible to study it by detecting the thermal processes in semiconductors. In this paper, the dynamics of nonradiative recombination has been investigated by means of the transient grating (TG) method with a nanosecond pulsed laser. The heat dynamics can be assessed by measuring the photo-induced change of refractive index. The TG method is one of the third order nonlinear spectroscopic technique.[1] Until now, this method has been used to detect the optical properties of semiconductor at the very fast region with picosecond or femtosecond pulse lasers. [2-5] However, the heat dynamics in semiconductors by the TG method with a nanosecond pulsed laser have not been investigated.

In this paper, this method was used to detect the nonradiative processes of carriers and/or excitons of ZnSe and GaN-based semiconductors, which are very important materials for light source with blue-green spectral region. Recently, it was found that the dislocation in ZnSe heteroepitaxial layer on GaAs substrate reduced the device lifetime and the emission efficiency.[6] the dislocation in ZnSe heteroepitaxial layer on GaAs substrate reduced the device lifetime and the emission efficiency. This fact suggests that the dislocations act as active centers for nonradiative recombination of carriers and/or excitons, and the excess energy generated by this process gives rise to dark spots originating from the multiplication of dislocations. Now, ZnSe substrate with an etch pit density as low as 10^4 cm^{-2} is commercially available. Some group developed the technique of the homoepitaxial growth of ZnSe on ZnSe substance, which is known of the drastically strong emission properties than that of the heteroepitaxial layers.[7-10]

On the other hand, GaN-based semiconductors have very strong emission property in spite of high threading dislocation density (10^8-10^{10} cm^{-2}). Some group studied the relationship between the threading dislocation and the emission efficiencies probed by the CL mapping, or site selective time-resolved PL and so on.[11-13] 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. [11-13]

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.

Experimental and method

The experimental set up for the TG technique was already published elsewhere.[14] Configuration of the excitation and probe beams of the TG method was shown in figure 1. The frequency tripled beam of Nd:YAG laser (Spectra Physics DC-11; λ=355nm) was used for excitation. The interference pattern is created by crossing two excitation beams in the sample materials. The excited area releases the heat by the nonradiative recombination of carriers and the temperature of

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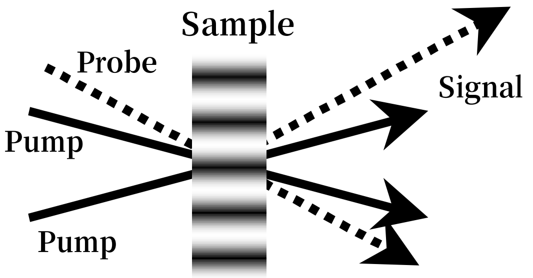

Fig. 1 Configuration of the excitation and probe beams of the Transient grating (TG) method.

the sample is modulated (thermal grating). Optical properties of the materials (diffractive index and absorbance) are also modulated by the thermal grating. Such modulation of optical properties is similar to the refractive grating. A probe beam from a He-Ne laser (633nm) was partly diffracted (TG signal) by these gratings. 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^{o}C).

Structures of the samples used in this paper are ZnSe (0.9μm) homoepitaxial layer and ZnSe (0.14μm) /$Zn_{0.75}Cd_{0.25}Se$(5nm) /ZnSe(0.9μm) single quantum well (SQW) on ZnSe substrate both of which are grown on bulk ZnSe substrate by molecular beam epitaxy (MBE). The growth technique of homoepitaxial growth was similar to Ref. 9-10. 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 deposition (MOCVD). The detail growth condition has been reported elsewhere[15]

Results 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 space are 4^{o} and 4.7μm, respectively. These signals rise immediately within the excitation pulse (few nanosecond) and decay within few tens nanosecond. This signal is due to the modulation of carrier densities and temperature (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. The intensity and time profile of the TG signals contain information on the amount of the released heat and on the thermal conductivity. The TG signal intensity is given by the sum of the square of the refractive index change and absorbance change.[16] 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 the refractive index change. Therefore, we can obtain information on the efficiencies of the nonradiative recombination of carriers from the intensity of the TG signals. The signal intensities of ZnSe were much larger than that of ZnCdSe/ZnSe SQW. This result suggests that the heat released by the nonradiative recombination of carries in ZnSe should be larger than that in SQW, showing that the efficiency of the nonradiative recombination in ZnSe is larger than that in SQW. This result is reasonable because the internal quantum efficiency of PL in SQW is much larger than that in ZnSe as observed by the temperature dependence of the PL intensity.[17]

The profile of the TG signal in ZnSe showed exponential time dependence. When the heat was created by the nonradiative recombination after the photoexcitation of the grating light, the increase of temperature depending on both time and space $\delta T(x, t)$ is given by solving the Fourier's diffusion equation as shown below

$$dT(q, t) = dT(q, 0) \exp(-D_{th} q^2 t) \qquad (1)$$

D_{th} is the thermal diffusivity given by $D_{th}=\lambda_c/\rho C_p$ (ρ, C_p, and λ_c are the density, the heat capacity and the thermal conductivity of material). $\delta T(q, t)$ is the q-component of the Fourier transformation of $\delta T(x, t)$.

Eq. (1) indicates that the decay profile of the TG signals should be fitted by a single exponential function. The diffraction efficiency is proportional to the square of refractive index change due to the increase of the temperature (ΔT). Therefore, from the pre-exponential factor and the decay rate constant, we can obtain ΔT by the nonradiative recombination and the thermal diffusivity (D_{th}). D_{th} is obtained as 0.084 cm^{2}s^{-1} and 0.41 cm^{2}s^{-1} for ZnSe and GaN, respectively. D_{th} of SQW was the same as that of ZnSe, though the signal intensity was different. 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 $D_{th}=\lambda_c/\rho C_p$. By using the literature values (λ_c=0.19 Wcm^{-1}K^{-1}, ρ=5.266 gcm^{-3}, and C_p=0.0086 calg^{-1}K^{-1} as ZnSe, λ_c=1.3 Wcm^{-1}K^{-1}, ρ=6.095 gcm^{-3}, and C_p=9.745 calmol^{-1}K^{-1} as GaN), D_{th} was calculated as D_{th}=1.00 cm^{2}s^{-1} and 0.44 cm^{2}s^{-1} for ZnSe and GaN, respectively. These values are close to the experimental one.

To elucidate the more detail information on the nonradiative recombination, we measured the excitation energy dependence of the TG signals as shown in figure.3. The straight lines are guide for eyes. In contrast to the case in GaN, ΔT in ZnSe and ZnCdSe/ZnSe SQW was saturated under the high excitation energy region. This fact probably suggests that photo-generated carriers or excitons in ZnSe-based semiconductors are more easily trapped by the nonradiative

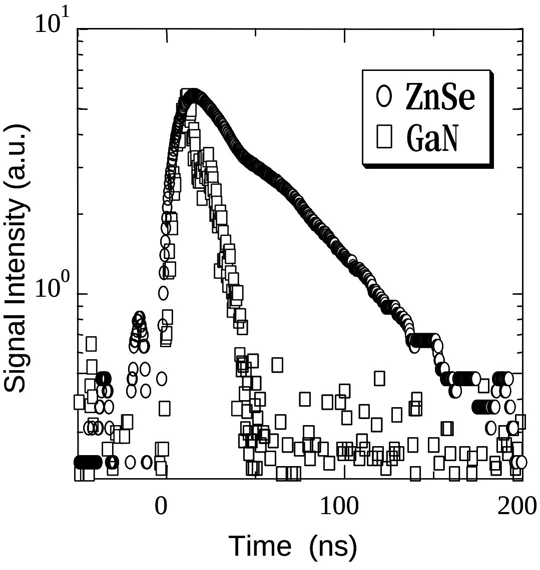

Fig. 2 Time profile of the TG signal of ○ZnSe and □ GaN epitaxial layer at room temperature.

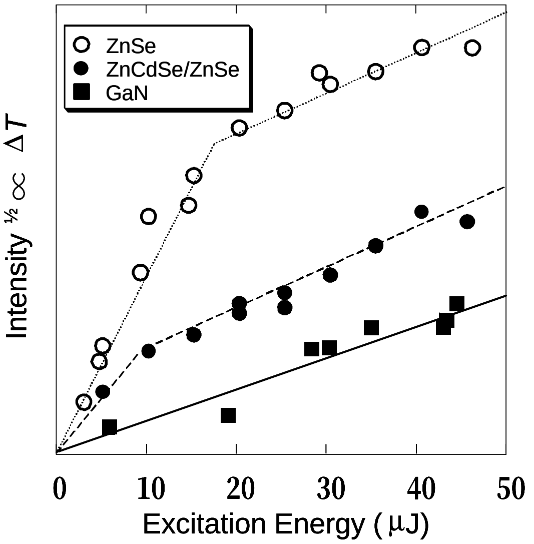

Fig. 3 Excitation energy dependence of the root square of the TG signals from the sample of ○ZnSe, ●ZnCdSe/ZnSe QW and ■GaN

recombination centers, resulting in the lower threshold carrier density for the saturation. It was also found that the saturation behavior in SQW takes place at lower energy than that in ZnSe epitaxial layer. This can not only be attributed to the higher concentration of nonradiative recombination centers in ZnSe because the carrier density in SQW would be higher than that in ZnSe, as can be understood as the photo-generated carriers in ZnSe cladding layer would be effectively captured to the narrow $Zn_{0.75}Cd_{0.25}Se$ well layer (5nm). Such saturation effect should be a reason for the higher emission intensity in the ZnSe-based semiconductors. Time resolved PL spectroscopy also reveal the effect of nonlinear enhancement on PL intensities in ZnSe homoepitaxial layer and ZnCdSe/ZnSe SQW near room temperature.[17] This effect supports the model of the saturation effect of the nonradiative centers in ZnSe-based semiconductor..

On the other hand, it was found that the nonradiative center in GaN was not saturated. This fact should be reasonable because GaN has much more dislocation in the crystals than that in ZnSe. However, GaN-based semiconductor have very very strong emission properties. 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 spacially resolved PL spectroscopy.[18] As mention 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.

In 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 ZnSe and GaN based semiconductors. We found that the nonradiative dynamics is different between ZnSe and GaN although the quantum efficiencies are comparable each other. 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. Such an approach is in progress.

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References

1. Eichler, P. Gunter, and D. W. Pohl, Laser-Induced Dynamic Grating, **1986**, (Springer, Berlin, 1986).
2. A. J. Fischer, D. S. Kim, J. Hays, W. Shan, J. J. Song, D. B. Eason, J. Ren, J. F. Schetzina, H. Luo, J. K. Furdyna, Phys. Rev. B, **1994**, 50, 17643.
3. (a) D. S. Kim, A. J. Fischer, J. Hays, W. Shan, J. J. Song, D. B. Eason, J. Ren, J. F. Schetzina, Appl. Phys. Lett., **1994**, 65, 1534: (b) A. J. Fischer, D. S. Kim, J. Hays, W. Shan, J. J. Song, D. B. Eason, J. Ren, J. F. Schetzina, H. Luo, J. K. Furdyna, Z. Q. Zhu, T. Yao, J. F. Klem, W. Schäfer, Phys. Rev. Lett., **1994**, 73, 2368.
4. J. Wang, D. C. Hutchings, A. Miller, E. W. Van Stryland, J. Appl. Phys., **1993**, 73, 4746.
5. B. Taheri, J. Hays, and J. J. Song, Appl. Phys. Lett. **1996**, 68, 587.
6. S. Guha, H. Munekata and L. L. Chang, J. Appl. Phys., **1993**, 73, 2294.
7. J. C. Werkhoven, B. J. Fitzpatrick, S. P. Herko, R. N. Bhargava, P. J. Dean, Appl. Phys. Lett., **1981**, 38, 540.
8. J. (a) T. Yodo, T. Koyama, K. Yamashita, J. Appl. Phys. 64 (1988) 2403: (b) T. Yodo, T. Koyama, H. Ueda, K. Yamashita, J. Appl. Phys., **1989**, 65, 2728.
9. J. T. Ohno, A. Ohki, T. Matsuoka, Jpn. J. Appl. Phys., **1997**, 36, L190.
10. J. A. Ohki, T. Ohno, T. Matsuoka, Y. Ichimura, Electron. Lett., **1997**, 33, 990.
11. T. Mukai, K. Takekawa, S. Nakamura, Jpn. J. Appl. Phys, **1998**, 37, L839.
12. T. Sugahara, M Hao, Y. Naoi, S. Tottori, K. Yamashita, K. Nishita, K. Nishino, L. T. Romano, S. Sakai, Jpn. J. Appl. Phys. **1998**, 37, L398.
13. S. Chichibu, H. Marchand, M. S. Minsky, S. Keller, P. T. Fini, J. P. Ibbetson, S. B. Fleischer, J. S. Speck, J. E. Bowers, E. Hu, U. K. Mishra, S. P. Denbaars, T. Deguchi, T. Sota, S. Nakamura,. Appl. Phys. Lett. **1999**, 74, 1460.
14. M. Terazima, K. Okamoto, N. Hirota, J. Phys. Chem., **1993**, 97, 5188.
15. S. Nakamura, Jpn. J. Appl. Phys., **1991**, 30, L1705.
16. (a) H. Kogelmik, Bell. Syst. Tech. J., **1969**, 48, 2909: (b) T. K. Gaylord, M. G. Mohatam, Appl. Phys., **1982**, B28, 1.
17. K. Okamoto, Y. Kawakami, Sg. Fujita, *to be published*
18. T. Izumi, Y. Narukawa, K. Okamoto, Y. Kawakami, Sg. Fujita, S. Nakamura, J. Luminescence **2000**, 87, 119.