Journal of Photoscience (2000), Vol. 7(1), pp. 27 – 30

Temperature Dependence of Excitonic Transitions in GaN Grown by MOCVD

Guangde Chen[1], Jingyu Lin[2], Hongxing Jiang[2], Jung Hwan Kim[3], Sung Eul Choi[4]*
[1]Department of Applied Physics, Xi'an Jiaotong University, Xi'an 710049, P. R. China
[2]Department of Physics, Kansas State University, Kansas 66506, USA
[3]Department of Physics, Dongeui University, Pusan 614-714, South Korea
[4]Department of Physics, University of Inchon, Inchon 402-749, South Korea

The Photoluminescence (PL) measurement results of a very good quality GaN sample grown by metalorganic chemical vapor deposition (MOCVD) are reported. The temperature dependences of peak position, emission intensity, and the full width at half maximum (FWHM) of free-exciton (FX) A and B are presented. Our results show the fast thermal quenching of FX transition intensities and predominantly acoustic phonon scattering of emission line broadening. The transition-energy-shift following the Varshni's empirical equation, and by using it to fit the data, $E_{A1}(T) = 3.4861$ eV - $6.046 \times 10^{-4} T^2 / (620.3 + T)$ eV, $E_{B1}(T) = 3.4928$ eV - $4.777 \times 10^{-4} T^2 / (408.2 + T)$ eV and $E_{A2} = 3.4991$ eV - $4.426 \times 10^{-4} T^2 / (430.6 + T)$ eV for A(n=1), B(n=1), and A(n=2) are obtained respectively.

key words: Photoluminescence, GaN, Metalorganic chemical vapor deposition (MOCVD), Free-exciton

GaN-based wide band gap semiconductor materials have attracted extensive attention in recent years mainly due to their many potential applications in optoelectronics, in which they directly result in blue-ultraviolet (UV) light emitting diodes (LEDs) and laser diodes (LD) [1,2]. There has been a considerable amount of research effort directed towards the preparation of high quality of GaN-based materials and devices, and also to the understanding of their fundamental physical properties [3,4,5]. The excitonic transitions have been recognized as the most important optical processes in GaN due to its LD application [6,7].

Several papers have been published on the temperature dependence of the near energy gap transitions in GaN [4,9], however, the results reported vary with the samples prepared by various growth techniques as well as different measurement methods, and lack detailed investigations on the temperature-dependent of emission intensities, peak positions and the full width at half maximum (FWHM) about free-exciton (FX) recombination of higher quality single crystal GaN sample. In this paper, we report our photoluminescence (PL) measurement results of temperature dependence of FX [A(n=1), B(n=1) and A(n=2)] recombination transitions in a very good quality GaN single crystal film grown by MOCVD, and discuss FX emission intensities, peak positions, and the FWHM varying with temperatures. The results show the quick thermal quenching of FX transition intensities, predominantly acoustic phonon scattering of FX emission line broadening and the good fitted values of emission line peak positions which vary with temperatures following the Varshni's empirical equation.

The GaN sample used in our experiment is of n-type wurtzite structure single crystal grown by low-pressure MOCVD technique prior to the deposition of the GaN layer a thin 50 μm AlN buffer layer was grown on the sapphire (Al_2O_3) substrate. The room temperature electron carrier concentration is about $5.0 \times 10^{16}/cm^3$ which was determined by Hall measurements.

For our PL measurements, the main experimental set up is shown in Fig. 1. The sample was attached to a copper sample holder and mounted inside a closed-cycle He refrigerator with the temperature variation from 10 K to 320 K.

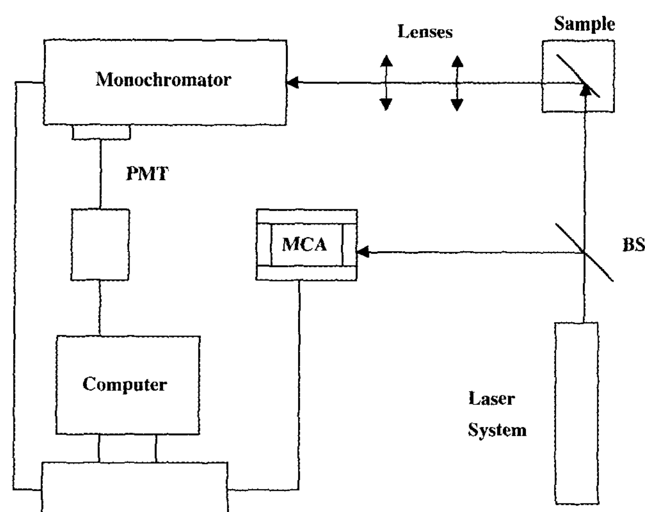

Figure 1. The experimental block diagram of photoluminescence measurement.

*To whom correspondence should be addressed.
E-mail: schoi@lion.inchon.ac.kr
Received 15 February 2000; accepted 20 March 2000

The PL spectra were collected in a reflecting mode. Excitation pules of 7 ps at the repetition rate of 9.5 MHz were provided by a cavity-dumped dye laser with Rhodamine 6G solution, which was pumped by a Nd^{3+}:YAG laser with a frequency doubler. The output from the dye laser was frequency doubled provide tunability in the UV region (up to 4.5 eV). A single-photon counting system and a grating monochromator were used to measure the PL spectra. In the block diagram of Fig. 1, the MCA represents the Multichannel Analyzer, and the PMT means the Photo multiplier Tube.

The continuous-wave (cw) PL spectra of the sample at several representative temperatures are shown in Fig. 2. There is nearly a single transition line of intrinsic FX A (n=1, ground state which was assigned by several papers previously [7,9]) with the peak energy at 3.4857 eV and the FWHM is only 1.81 meV at the temperature 10 K, which represents the single crystal GaN sample under investigation is of very high quality. The very small peak at the energy peak 3.4926 eV is FX B(n=1). The inset in Fig. 2 shows the relative intensity variations of A and B excitonic transitions at three representative temperatures. An emission line, which is about 14 meV higher than that of the A(n=1) emission line, appears when the temperature increases to T > 40 K. We assigned this emission line as the first excited state A(n=2) due to its peak energy position away from that of A(n=1). The absolute transition intensities of the excitonic emission lines decrease with increasing temperature as it is expected. We plotted the temperature dependence of emission intensities of FX A(n=1) and FX B(n=1) in Fig. 3, which shows the fast thermal quenching of FX transition intensities. We have not got a suitable formula to fit those data well, because the intensities decrease very quickly especially below 60 K. The insets in Fig. 3 are the semilogarithmic scale of the integrated intensity of FX A and FX B emission lines versus temperatures, which show clearly an activated behavior at the range of temperatures.

It is worthwhile to mention from Fig. 2 and Fig. 3 that the relative intensity ratio of FX B to FX A emission line increases as temperature increases, although both absolute emission intensities decrease with the increase of temperature. In particular, at the temperatures above 80 K, the intensity of FX B transition is higher than that of FX A transition, and this behavior keeps going up to room temperature. To our best knowledge, this phenomenon is reported for the first time and has a little difficulty to explain and justify now. The most probable explanation for this phenomenon might be due to either their different thermal quenching mechanism with temperatures or a stronger coupling effect between them because of FX motion in crystal and interactions between

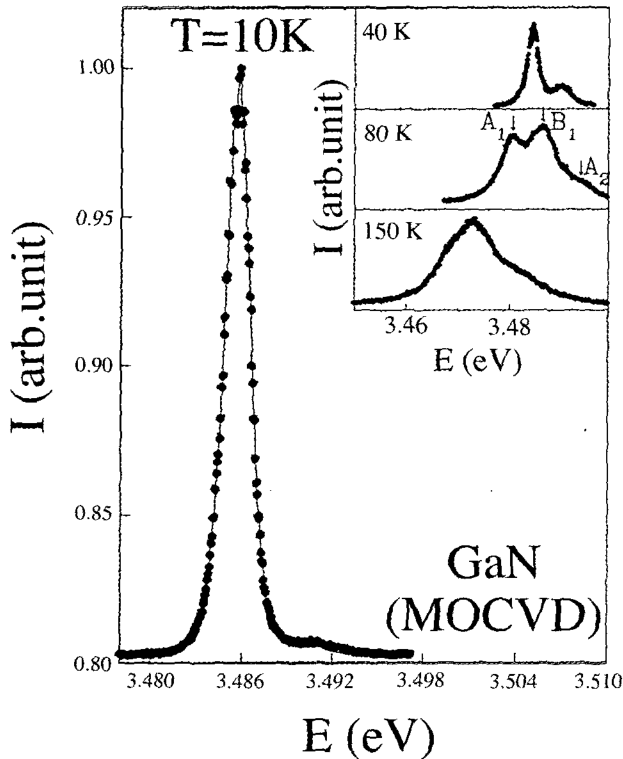

Figure 2. Continuous Wave (CW) photoluminescence spectra of an unintentionally doped n-type GaN at T ≈ 10 K. The inset shows the relative intensity variation of different free excitons at the representative temperatures.

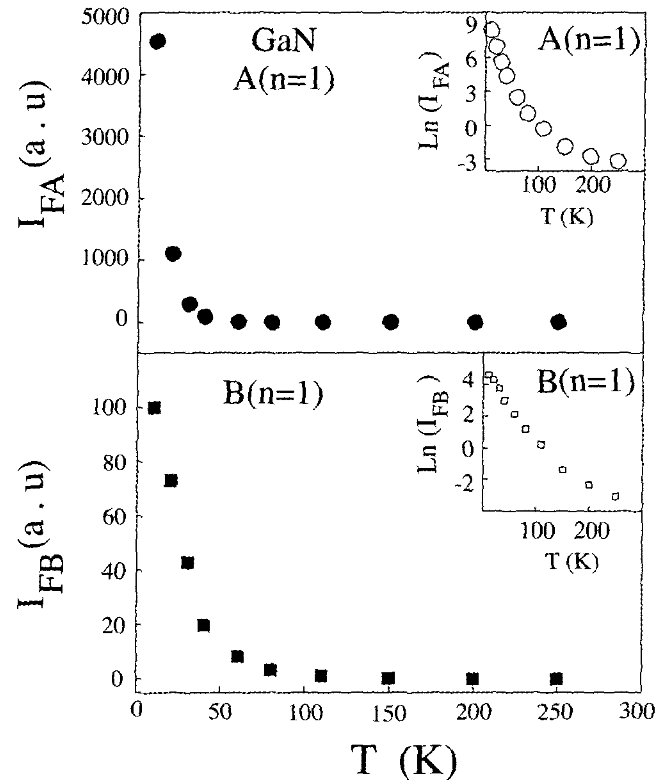

Figure 3. The temperature dependence of transition intensities of FX A(n=1) and B(n=1). The insets are the semilogarthmatic scale of the integrated intensity of FX A(n=1) and B(n=1) versus temperatures.

FXs and phonons. To confirm and justify, further detailed investigations both in experimental and in theoretical research might be needed.

The peak positions of the three excitation emission lines shifted to lower energy side with the temperature increased as shown in Fig. 3 (dots). As far as GaN was expected to have a high Debye temperature and a temperature dependence band gap variation [11,12], the overall feature here was consistent with the previous results [9]. To fit the temperature dependence of peak positions of FX emission lines, we use the Varshini's empirical equation

$$E_g(T) = E(0) - \alpha T^2 / (T + \beta) \quad (1)$$

where E(0) is the FX transition energy at T = 0 K, and α, β are the constants referred to as Varshini thermal coefficients (β also corresponds to the Debye temperature θ which was estimated to be about 600 K in GaN theoretically[12]).

The solid lines in Fig. 4 are the least-square fittings of the experimental data by using Eq. (1). The fitted values obtained from the best fitting are $E_{A1}(0)$ = 3.4861 eV, $\alpha = 6.046 \times 10^{-4}$ eV/K, β = 620.3 K for the ground state of FX A; $E_{B1}(0)$ = 3.4928 eV, $\alpha = 4.777 \times 10^{-4}$ eV/K, β = 408.2 K for the ground state of FX B; and $E_{A2}(0)$ = 3.4991 eV, $\alpha = 4.426 \times 10^{-4}$ eV/K, β = 430.6 K for the first excited state of FX A.

The FWHM of the FX emission lines increases with temperature increasing due to increased exciton-phonon interaction. We plotted the FWHM (Γ) of FX A and FX B transition lines as the function of temperatures in Fig. 5, which shows that Γ increases linearly with temperatures. The temperature dependence of the emission line width caused by exciton-phonon interactions has a form [13,14].

$$\Gamma(T) = \Gamma_0 + \gamma_{LA}T + \gamma_{Lo} / [\exp(E_{Lo} / kT) - 1] \quad (2)$$

where Γ_0 represents the line broadening due to temperature-independent mechanisms (such as Auger process, impurity, surface scatting and inhomogeneous etc.); $\gamma_{LA}T$ arises from the interaction between longitudinal acoustic (LA) phonon modes of the lattice and excitons, γ_{LA} is the LA coefficient; the third term on the right side of Eq. (2) stems from the interaction between longitudinal optical (LO) phonon modes of lattice and excitons, γ_{LO} is the width parameter and E_{LO} is the LO phonon energy of GaN.

The linear behavior shown in Fig. 5 implies that the exciton-LA phonon interaction dominates in the FX emission line broadening in GaN, which is consistent with the interband tran-

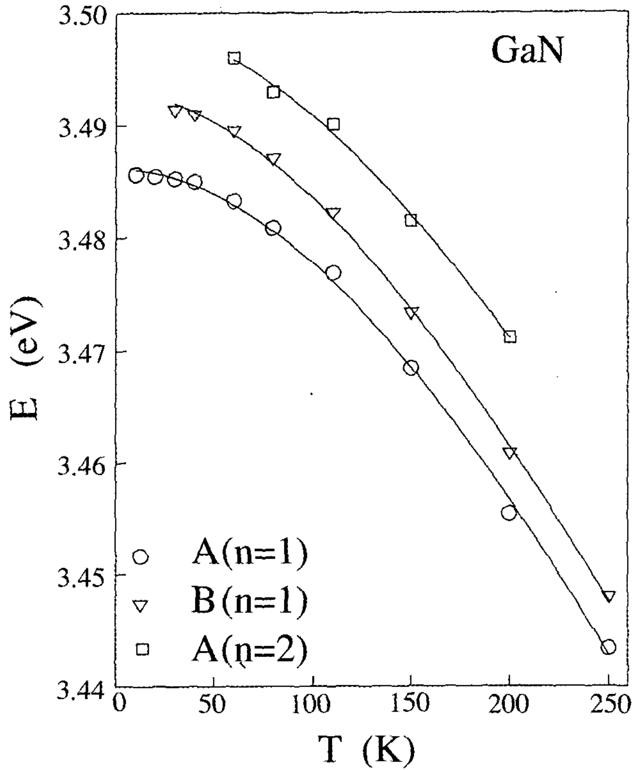

Figure 4. The temperature dependence of peak positions of A(n=1), B(n=1) and A(n=2) excitonic transition lines as obtained from Fig. 2. The solid lines are the least-squares fitting of the data with Eq. (1).

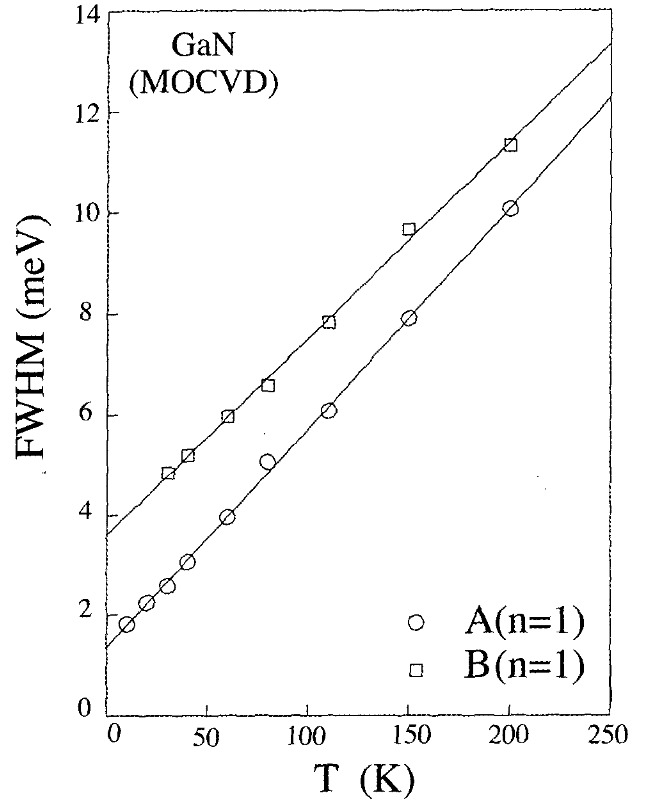

Figure 5. The full width at half maximum (FWHM) of FX A(n=1) and B(n=1) transitions as a function of temperature. The dots are the experimental data, and the solid lines are the least-squares fitting of a linear relation with temperature of Eq. (2).

sition broadening reported previously [15] , and also is consistent with FX emission broadening reported in CdS [16]. The solid line in Fig. 5 designate fits of the data assuming the linear relation of the form (neglecting the exciton-LO phonon interaction term)

$$\Gamma_0 = \Gamma_0 + \gamma T \quad (3)$$

The fitted values are Γ_0 = 1.3541 meV, γ = 0.04365 meV/K for FX A(n=1), and Γ_0 = 3.6171 meV, γ = 0.03891 meV/K for FX B(n=1) respectively. The results show clearly that the FX emission line width broadening in the GaN sample grown by MOCVD is predominantly determined by acoustic phonon scattering at least in the range of temperature from 10 K to 200 K.

In summary, the temperature dependence of free excitonic transitions including FX A(n=1), B(n=1), and A(n=2) are presented. The emission intensities for both FX A and FX B decrease very fast with the increase of temperatures. The interesting phenomenon is that the relative intensity ratio of FX B to FX A increases with temperature increasing and the ratio is larger than 1 at the temperature over 80 K. The FWHM of FX A(n=1) and FX B(n=1) present the linear relation with temperature and the predominantly acoustic phonon scattering. The peak position varies with temperature following the Varshini's empirical equation. By using the Varshini's equation to fit the experimental data, $E_{A1}(T)$ = 3.4861 eV - 6.046 $\times$ 10^{-4} $T^2/(620.3 + T)$ eV , $E_{B1}(T)$ = 3.4928 eV - 4.777 $\times$ 10^{-4} $T^2/(408.2 + T)$ eV and E_{A2} = 3.4991 eV - 4.426 $\times$ 10^{-4} $T^2/(430.6 + T)$ eV are obtained for A(n=1), B(n=1), and A(n=2) respectively.

Acknowledgments – This work was supported in part by the Science and Technology Police Institute through the Korea-China Scientists Exchange Program and also in part by the Chinese Education Commission Foundation for Excellent Young Teachers.

REFERENCES

1. Morkoc, H., S. Strit, G. B. Gao, M. E. Lin, B. Sverdlov and M. Burns (1994) *J. Appl. Phys.* **76**, 1363.
2. Asif Khan, M., M. S. Shur, J. N. Kuznia, Q. Chen, J. Burm and W. Schaff (1995) Temperature activated conductance in GaN/AlGaN heterostructure field effect transitors operating at temperatures up to 3000℃. *Appl. Phys. Lett.* **66**, 1083-1085.
3. Monemar, B. (1974) *Phys. Rev. B*, **10**(2), 676.
4. Logothetidis, S., J. petalas, M. Cardona and T. D.Moustakas (1994) Optical properties and temperature dependence of the interband transitions of cubic and hexagonal GaN. *Phys.Rev. B* **50**(24), 18017-18029.
5. Chen, G. D., M. Smith, J. Y. Lin, H. X. Jiang, A. Salvador, B. N. Sverdlov, A. Botchkarv and H. Morkoc (1994) *J. Appl. Phys.* **79**(5), 2675.
6. Yang, X. H., T. J. Schmidt, W. Shan, J. J. Song and B. Goldenberg (1995) Above room temperature near ultraviolet lasing from an optically pumped GaN film grown on sapphire. *Appl. Phys. Lett.* **66**, 1-3.
7. Chen, G. D., M. Smith, J. Y. Lin,H. X. Jiang, Su-Huai Wei, M. Asif Khan and C. J. Sun (1996) Fundamental optical transitions in GaN. *Appl. Phys. Lett.* **68**(20), 2784 -2786.
8. Pankove, J. I. (1971) Optical Processes in Semiconductors (Dover), New York, Chap. 6.
9. Shan, W., T. J. Schmidt, X. H. Yang, S. J. Hwang, J. J. Song and B. Goldenberg (1995) Temperature dependence of interband transitions in GaN grown by metalorganic chemical vapor deposition. *Appl. Phys. Lett.* **66**(8), 985-987.
10. Pankove, J. I., J. E. Berkeyheiser, H. P. Maruska and J. Wittke (1970) *Solid State Commun.* **8**, 1051-1053.
11. Varshini, Y. P. (1967) *Physica* **34**, 149.
12. Willardson, R. K. and R. C. Beer (1966) Academic Press, New York, **2**, 53.
13. Rudin, S., T. L. Reinecke and B. Segall (1990) Temperature-dependent exciton linewidths in semiconductors. *Phys. Rev. B* **42**, 11218-11231.
14. Srinivas, V., Y, J. Chen and C. E. C. Wood (1994) *Solid State Commun.* **89**, 611.
15. Logothetidis, S., J. petalas, M. Cardona and T. D.Moustakas (1994) Optical properties and temperature dependence of the interband transitions of cubic and hexagonal GaN. *Phys.Rev. B*, **50**(24), 18017-18029.
16. Gross, E., S. Permogorov and B. Razbirin (1966) *J. Phys. Chem. Solids*, **27**, 1647-1651.