Free excitonic transitions in GaN, grown by metalorganic chemicalvapor deposition

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M. Smith, G. D. Chen,[a)] J. Y. Lin, and H. X. Jiang
Department of Physics, Kansas State University, Manhattan, Kansas 66506-2601

M. Asif Khan, C. J. Sun, Q. Chen, and J. W. Yang
APA Optics, Inc., 2950 N.E. 84th Lane, Blaine, Minnesota 55449

The dynamic processes of the free excitonic transitions in GaN grown by metal-organic chemical-vapor deposition (MOCVD) have been studied. The recombination lifetimes of the A and B excitons have been measured at different temperatures and excitation intensities, from which radiative recombination lifetimes of about 0.35 and 0.3 ns for the A and B excitons, respectively, have been obtained. An increase in excitation power has resulted in a drastic enhancement in the radiative decay rate as well as in the exciton photoluminescence quantum yield, suggesting the excitonic transitions may provide gain for laser actions in GaN. The high quality as well as high purity of the investigated MOCVD sample has been demonstrated by the observations of (1) the free A- and B-excitonic transitions, (2) excited states of the free excitons, (3) narrow free excitonic emission linewidths (1.7 meV at 10 K), (4) low electron concentration, and (5) high electron mobilities ($\sim$600 cm^2/V s). © *1996 American Institute of Physics.* [S0021-8979(96)00409-X]

I. INTRODUCTION

GaN and its alloys (AlGaN and InGaN) have been recognized as technologically very important but relatively less understood materials. They have recently attracted considerable interest due to their applications for optical devices which are active in the blue and ultraviolet (UV) wavelengths and electronic devices capable of operation at high temperatures, high power level, and harsh environments.[1–5] However, the understanding of their fundamental optical properties is still far form complete. In this paper we report time-resolved photoluminescence results of free excitonic transitions in a nominally undoped n-type GaN epitaxial layer grown by metal-organic chemical-vapor deposition (MOCVD). Systematic dependencies of the free exciton recombination lifetimes on temperature and excitation intensity have been measured, from which the radiative recombination lifetimes of the A and B excitons in MOCVD-grown GaN have been obtained. Our experimental results have demonstrated that the material quality, which has been a main problem for GaN, has been improved to a significant degree. This allows the investigation of fundamentally important optical processes as well as basic parameters in GaN. An understanding of the fundamental optical transitions and their dynamic processes will provide important information for improving sample qualities as well for design and optimize optoelectronic devices.

II. EXPERIMENT

The wurtzite, nominally undoped n-type GaN sample used here was grown on a sapphire substrate by using low-pressure MOCVD. The detailed growth processes and structural and electrical characterizations have been reported pre-

viously.[6] The thickness of the GaN epitaxial layer is about 3.8 μm. A room-temperature (RT) electron concentration (due to unintentional doping) of about 5×10^{16} cm^{-3} and electron mobility of 600 cm^2/V s were determined by Hall measurements. The excitation source was a pulsed (7 ps pulse width at 9.5 Mhz) dye laser with a frequency doubler, which has an average power of about 20 mW, a tunable photon energy up to 4.5 eV, and a spectral width of about 0.2 meV. For luminescence spectra measured at different excitation intensities, the laser intensity was controlled by a set of UV neutral density filters with different values of optical density D, and was thus proportional to 10^{-D}.

III. RESULTS AND DISCUSSION

Figure 1 shows photoluminescence spectra of the GaN sample measured at several temperatures from $T=10$ to 150 K. The spectral peak positions of all observed emission lines shift toward lower emission energies as the temperature increases, following the temperature variation of the band gap. Several emission lines can be clearly resolved from Fig. 1. At $T=10$ K, only one dominant transition line at about 3.4857 eV can be observed, which is due to the free A-exciton ($n=1$) recombination. There is a weak transition line in the 10 K spectrum at the higher-energy side of the A-exciton ($n=1$) transition, which becomes very clear at $T=40$ K. This line is about 6.4 meV above the A-exciton ($n=1$) line and becomes the dominant emission line at temperatures above 80 K. This line is due to the free B-exciton ($n=1$) transition. As temperature increases further (see 80 K spectrum), an additional transition line which is about 13.7 meV above the A-exciton ($n=1$) line starts to emerge. We assign this line to the recombination of the first excited state of the A exciton ($n=2$) based on its spectral position, emission intensity, and temperature dependence. The C-exciton transition is expected to lie about 40 meV above the A-exciton line according to a recent photoreflectance

[a)]Permanent address: Department of Applied Physics, Xi'an Jiaotong University, People's Republic of China.
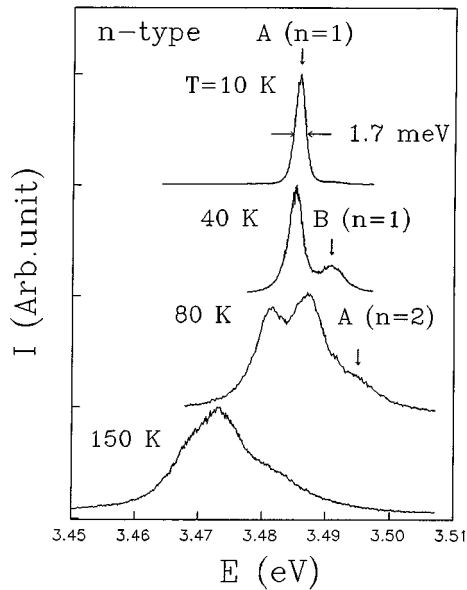
FIG. 1. Photoluminescence spectra of excitonic transitions measured at several temperatures from $T = 10$ to 150 K. Each spectrum has been normalized to its maximum intensity and shifted vertically for a clear presentation. The arrows for A($n=1$), B($n=1$), and A($n=2$) indicate the transitions of the ground-state A exciton, B exciton, and the excited-state A exciton.

FIG. 2. Temperature dependence of the integrated luminescence intensities of (a) A($n=1$) and (b) B($n=1$) transitions together with the lease-squares fit (the solid curves) of data with Eq. (1).

measurement[7] and our recent calculation based on a local-density approximation (LDA).[8] Our assignments are based on

(a) time-resolved photoluminescence measurements which reveal that the dynamical behaviors of the 3.4857 eV line and that 6.4 meV above are different from that of the neutral-donor-bound exciton transition observed in other samples, and

(b) emission spectra of other samples with higher electron concentrations, in which both the I_2 and the A-exciton ($n=1$) transitions at the corresponding energy positions are observable.[9]

These assignments have been further confirmed by the fact that the emission intensities of the observed transition lines depend strongly on the excitation light polarization direction, as expected for free excitons.[10]

Several unique features can be observed in the emission spectra shown in Fig. 1. First, the transition line due to the recombination of the first excited state of the A exciton ($n=2$), which has been observed in high-quality GaN grown by a newly developed reactive molecular-beam epitaxy (MBE),[11] has never been observed previously in MOCVD-grown GaN layers. Second, the neutral-donor-bound exciton I_2 at about 3.474–3.478 eV (at $T = 10$ K) depending on sample quality and carrier concentration, which is usually the dominant emission line in high-quality samples as reported previously by many groups, is absent. Third, the full width at half-maximum (FWHM) of the 10 K spectrum is only 1.7 meV, which is the narrowest linewidth reported for free excitonic transitions in GaN. It is well known that at low temperatures (near 1 K) in highest-quality crystals (CdS and GaAs crystals, for example), the typical FWHM is about 1
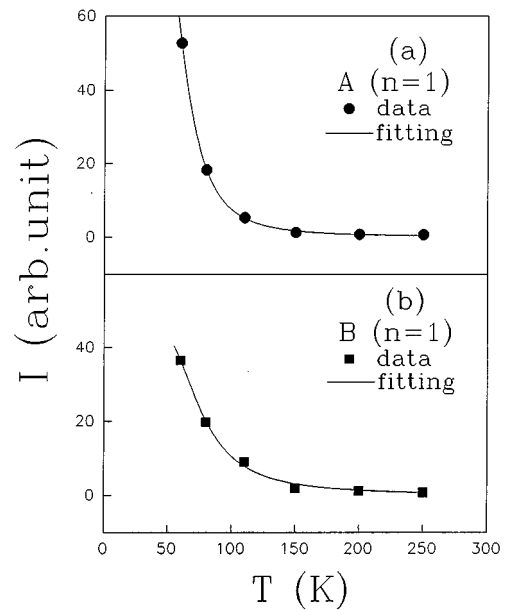
meV for free excitonic transitions and is about 0.1 meV for bound exciton transitions (e.g., I_2).[12] So the FWHM observed at 10 K here represents almost the intrinsic linewidth of the free excitonic transitions in GaN. These results together with the observations of the low electron concentration and high electron mobility have demonstrated the high quality as well as high purity of the investigated GaN crystal.

The energy differences between the A($n=1$) and B($n=1$) excitons,

$$\Delta E_{AB} = E[A(n=1)] - E[B(n=1)] = 6.4 \text{ meV},$$

and between the ground ($n=1$) and the excited state ($n=2$) of the A excitons, $E_{12}^A = 13.7$ meV), are independent of temperature (not shown) as expected. From the relation $E_{12}^A = (1 - 1/2^2)E_b^A$, with E_b^A being the binding energy of the A exciton, we obtain $E_b^A = 18.3$ meV. From the peak position of the A($n=1$) transition (3.4857 eV), we obtain the energy band gap of GaN at $T = 10$ K to be about

$$E_g = 3.4857 + 0.0183 = 3.504 \pm 0.001 \text{ eV},$$

which is exactly the current accepted value. This supports further our assignment for the ground and excited states of the A-exciton recombination. The A-exciton binding energy of about 28 meV obtained in the 1970s was overestimated due to the relatively low sample quality which causes broadening of and overlap between the I_2 and A-exciton transition lines.[13] We thus obtain a value of 42 Å for the A-exciton Bohr radius by taking the low-frequency dielectric constant to be 9.5.[13] The binding energy of the A exciton observed here is slightly lower than a value of 20 meV observed in a high-quality GaN sample grown by the new MBE technique, which may be caused by different interface properties (such as strain) resulting from the two different growth methods as we have speculated previously.[11]
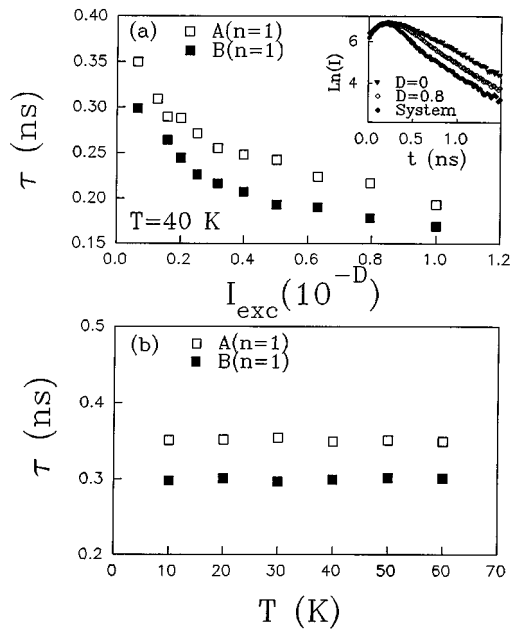
FIG. 3. (a) Excitation intensity $I_{exc}(\propto 10^{-D})$ dependence of the recombination lifetimes of the A($n=1$) and B($n=1$) excitonic measured at their respective spectral peak positions at 40 K. The inset shows the temporal responses of the A($n=1$) transition measured at two representative excitation intensities for $D=0$ and $D=0.8$. The detection system response to the laser pulses (7 ps) is also included in the inset and indicated as "system." (b) Temperature dependence of the recombination lifetimes of (a) A($n=1$) and (b) B($n=1$) excitonic transitions measured at their respective spectral peak positions and at low excitation intensities.

The integrated photoluminescence emission intensities of both A- and B-exciton transitions decrease with an increase of temperature and are thermally activated and can be well described by[14]

$$I(T) = I_0 / [1 + C \exp(-E_0/kT)], \qquad (1)$$

as shown in Fig. 2 for (a) A($n=1$) and (b) B($n=1$) transitions. The fitted values of the activation energy E_0 are $E_0^A = 21$ meV and $E_0^B = 20$ meV for the A and B excitons, respectively. The slight difference between the activation energy ($E_0 \approx 21$ meV) estimated from Eq. (1) (which is valid for a single energy level) and the binding energy ($E_b = 18.3$ meV) of the A exciton may be due to the coexistence of A, B, and C valence bands, which should modify Eq. (1). Results in Fig. 2 clearly show that the temperature dependence of the A- and B-exciton emission intensities is due to the formation of fewer excitons at higher temperatures.

Because of the absence of the I_2 line and well-separated A($n=1$) and B($n=1$) emission lines, we have been able to measure directly the recombination lifetimes of the A and B excitons by employing time-resolved emission spectroscopy. The inset of Fig. 3(a) shows the decay of photoluminescence measured at the A-exciton transition peak at 40 K for two representative excitation intensities. The detection system response to the laser pulses is also included and indicated as "system," which is about 0.3 ns. With the use of a deconvolution technique developed by Photon Technology International, Inc. (PTI), the recombination lifetimes can be measured down to about 40 ps, as specified by PTI. From the

decay data, we can see that the exciton luminescence decays exponentially, $I(t) = I_0 e^{-t/\tau}$, where τ defines the recombination lifetimes. We have measured luminescence temporal responses at different temperatures, emission energies (both A and B excitons), and excitation intensities. In all cases the decay is single exponential.

In the main figure of Fig. 3(a) we have plotted the recombination lifetimes of the A and B excitons measured at their respective emission peak positions at 40 K as functions of relative excitation intensity $I_{exc}(\propto 10^{-D})$. The B-exciton recombination lifetimes are about 15% shorter than those of the A excitons. The excitation intensity dependence of the recombination lifetime of the A($n=1$) transition has also been measured at $T=10$ K and similar results have been obtained. The lifetime progressively decreases as the relative excitation intensity increases. We attribute the observed behavior to the exciton–exciton interaction, which causes a reduction in the free exciton radiative recombination lifetime; however, such an interaction is absent at low free exciton densities. The radiative quantum efficiency η is directly related to the radiative recombination lifetime by $\eta = [1 + (\tau_r/\tau_n)]^{-1}$ where τ_r and τ_n denote, respectively, the radiative and nonradiative recombination lifetimes. Our results show that η is enhanced under the influence of the exciton–exciton interaction.[15] This is further supported by the observation that the photoluminescence quantum yield increases superlinearly with the excitation intensity in this sample. At the lowest excitation intensity, the recombination lifetimes are about 0.35 ns for the A excitons and 0.3 ns for the B excitons.

The temperature dependence of the recombination lifetime of (a) A($n=1$) and (b) B($n=1$) exciton measured at low power densities is shown in Fig. 3(b). The lifetimes of both A and B excitons are independent of temperature, which implies that radiative recombination is the dominant process at $T < 60$ K. Additionally, from the temperature-independent behavior of the recombination lifetimes we expect that their excitation intensity dependencies at different temperatures are the same as those shown in Fig. 3(a). Thus the recombination lifetimes obtained at low power densities represent the radiative recombination lifetimes for a single exciton. The results shown in Fig. 3 suggest that the radiative recombination lifetimes for single A and B excitons are about 0.35 and 0.3 ns, respectively. On the other hand, the radiative recombination lifetimes of A and B excitons in MBE-grown GaN is about 0.22 ns.[11] The slightly shorter exciton lifetimes observed in the MBE sample are consistent with the slightly larger exciton binding energies seen in the MBE sample. The observed free exciton radiative recombination lifetimes in GaN are much shorter than those in other semiconductors such as GaAs (Ref. 16) and CdS.[17]

The results of Fig. 3 also show that the radiative decay rate increases with an increase of excitation intensity for both A and B excitons due to exciton–exciton interaction, which has resulted in an enhanced exciton photoluminescence quantum yield in this sample. Such an interaction has been identified as one of the most important gain mechanisms in semiconductor laser materials.[15] There are evidences that excitons can provide gain in blue-green lasers based on the

ZnSe system, primarily attributing to the large exciton binding energies in ZnSe-based quantum wells.[18] The large binding energies of the free excitons in GaN together with our results here indicate that the free excitonic transitions may also provide gain for laser actions in GaN.

IV. CONCLUSIONS

In conclusion, free excitonic transitions in GaN grown by MOCVD have been studied at different conditions by time-resolved photoluminescence emission spectroscopy. The high quality as well as high purity of the investigated MOCVD sample have been demonstrated by the observations of

(1) the free A- and B-excitonic transitions,
(2) excited states of the free excitons,
(3) narrow emission linewidths (1.7 meV at 10 K) of the free excitonic transitions,
(4) low electron concentration, and
(5) high electron mobilities ($\sim$600 cm^2/V s).

We have been able to deduce important basic parameters including the A-exciton binding energy and the band gap from the photoluminescence emission spectra. Recombination lifetimes of the A and B excitons have been measured at different temperatures and excitation intensities, from which their radiative recombination lifetimes have been obtained. The photoluminescence quantum yield increases drastically with the excitation intensity. These results indicate that the excitonic transitions may provide gain for laser actions in GaN.

[1] H. Morkoç, S. Strite, G. B. Gao, M. E. Lin, B. Sverdlov, and M. Burns, J. Appl. Phys. **76**, 1363 (1994).
[2] M. A. Khan, M. S. Shur, J. N. Kuznia, Q. Chen, J. W. Burn, and W. J. Schaff, Appl. Phys. Lett. **66**, 1083 (1995).
[3] *Wide Bandgap Semiconductors*, edited by T. D. Moustakas, J. I. Pankove, and Y. Hamakawa, Mater. Res. Soc. Symp. Proc. 242 (MRS, Pittsburgh, PA, 1992).
[4] S. Nakamura, T. Mukai, and M. Senoh, Appl. Phys. Lett. **64**, 1687 (1994).
[5] R. Dingle and M. Ilegems, Solid State Commun. **9**, 175 (1971).
[6] M. Asif Khan, Materials Research Society Symposium, Boston, MA, November 27– December 1, 1995.
[7] W. Shan, T. J. Schmidt, X. H. Yang, S. J. Hwang, J. J. Song, and B. Goldbenberg, Appl. Phys. Lett. **66**, 985 (1995).
[8] G. D. Chen, M. Smith, J. Y. Lin, H. X. Jiang, S.-H. Wei, M. A. Khan, and C. J. Sun (unpublished).
[9] G. D. Chen, M. Smith, J. Y. Lin, H. X. Jiang, M. A. Khan, and C. J. Sun, Appl. Phys. Lett. **67**, 1653 (1995).
[10] R. Dingle, D. D. Sell, S. E. Stokowski, and M. Ilegems, Phys. Rev. B **4**, 1211 (1971).
[11] M. Smith, G. D. Chen, J. Z. Li, J. Y. Lin, H. X. Jiang, A. Salvador, W. K. Kim, O. Aktas, A. Botchkarev, and H. Morkoç, Appl. Phys. Lett. **67**, 3387 (1995).
[12] J. I. Pankove, *Optical Processes in Semiconductors* (Dover, New York, 1971), Chap. 6.
[13] Landolt–Börnstein, *Numerical Data and Functional Relationships in Science and Technology*, edited by P. Eckerlin and H. Kandler (Springer, Berlin, 1971), Vol. III.
[14] D. Bimberg, M. Sondergeld, and E. Grobe, Phys. Rev. B **4**, 3451 (1971).
[15] C. Klingshirn and H. Haug, Phys. Rep. **70**, 315 (1981).
[16] G. W.'t Hooft, W. A. J. A. van der Poel, L. W. Molenkamp, and C. T. Foxon, in *Excitons in Confined Systems*, edited by R. DelSole, A. D'Andrea, and A. Lapiccirella, Springer Proceedings in Physics (Springer, New York, 1988), p. 134.
[17] U. Heim and P. Wiesner, Phys. Rev. Lett. **30**, 1023 (1973).
[18] W. Huang and F. C. Jain, Appl. Phys. Lett. **66**, 1596 (1995).