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The mechanism of room-temperature (RT) intrinsic optical transition in high quality and purity GaN epilayer grown by metalorganic chemical vapor deposition (MOCVD) has been investigated. Our results show that the band-to-band instead of excitonic transition is the dominant transition in MOCVD grown GaN epilayer at RT. This conclusion is supported by the observation of the excitation intensity dependence of the photoluminescence emission peak position and by a model calculation. The band-to-band transition energy at RT at the limit of low carrier concentration has been determined to be 3.429 eV. Since the band-to-band transition is the dominant optical transition at RT, it thus suggests that the electron-hole plasma is most likely responsible for gain in GaN blue lasers similar to the case in other III–V semiconductor lasers. © *1997 American Institute of Physics.* [S0003-6951(97)00231-3]

GaN has recently been recognized as one of the most important semiconductors[1,2] due to its potential for many device applications, including UV-blue light emitting diodes (LEDs) and laser diodes (LDs). There has been a considerable amount of research effort directed toward the understanding of its optical properties. Many important band-edge transitions, including free and bound excitons, and band-to-impurity transitions have been investigated thoroughly in GaN epilayers as well as in quantum wells.[3–7] Among all the band-edge transitions, one important optical transition has not yet been identified in GaN epilayers is the band-to-band or free-electron to free-hole transition. One of the most important questions remains to be answered is that what is the dominant intrinsic optical transition in undoped GaN epilayers at room temperature (RT). In high quality and purity crystals, either the exciton or band-to-band transition is expected to be the dominant optical transition at RT depending on their radiative recombination rates and the exciton binding energy. However, a clear identification is not trivial since the exciton binding energy in III nitrides is about the RT thermal energy. Although the photoluminescence (PL) emission in GaN epilayers has been studied in GaN at RT, its exact mechanism has not yet been identified. In a Si doped GaN/AlGaN quantum well,[8] due to the effects of screening of ionized Si donors, the band-to-band transition has been observed at RT. From the fundamental physics point of view, the band-to-band transition provides direct information regarding energy gap as well as the interactions between the free electrons and holes. In the aspects of device applications, the band-to-band recombination is one of the most important optical processes to be utilized in many optoelectronic devices, including LEDs and LDs. On the other hand, understanding the mechanisms of optical transitions in GaN at RT is particularly important since most devices operate at RT. If the band-to-band transition is the dominant transition at RT in GaN as our experimental results and calculation indicate, then the formation of biexciton and excitonic molecules in GaN at RT under high carrier injection condition is difficult, which in turn implies that the electron-hole plasma (EHP) is most likely responsible for gain in GaN blue lasers similar to other III–V semiconductor lasers.[9]

In this letter, we report the observation and the properties of the band-to-band transition in GaN epilayers. The observed excitation intensity dependencies of the emission peak positions, the emission intensity, and the emission linewidth all indicate that the band-to-band transition is the dominant recombination process in metalorganic chemical vapor deposition (MOCVD) grown GaN epilayers at RT. With the identification of this important transition in the present study and the excitonic transitions in previous studies,[3–6] we have obtained a coherent picture for the fundamental optical transitions in GaN.

The wurtzite, nominally undoped high quality and purity *n*-type GaN epilayers used here were grown on a sapphire substrate by using low pressure MOCVD.[4] The thickness of the GaN epilayer was about 3.8 μm. A low RT electron concentration (due to unintentional doping) about 5×10^{16} cm^{-3} and high electron mobility of 600 cm^2/Vs were determined by Hall measurements. The laser system and experimental details have been described previously.[3,4]

Figure 1 shows the PL spectra of the GaN epilayer measured at several temperatures from $T = 30$ to 300 K. Narrow linewidth at low T and the absence of any impurity transitions again indicate the high quality and purity of the materials studied here. The spectral peak positions of the emission lines shift toward lower energies as T increases, following the temperature variation of the band gap. Several emission lines can be clearly resolved from the 30 K spectrum. The emission lines at about 3.4857 eV (*AX*) and 3.4921 eV (*BX*) are due to the recombination of the free *A*- and *B*-exciton ground state ($n = 1$), respectively.[3–5] The point we want to make from Fig. 1 is that it is difficult to follow the *A*- and *B*-exciton transition peaks from the temperature variation of the PL spectra. The energy difference between the excitonic and the band-to-band transitions is expected to be close to the exciton binding energy which is

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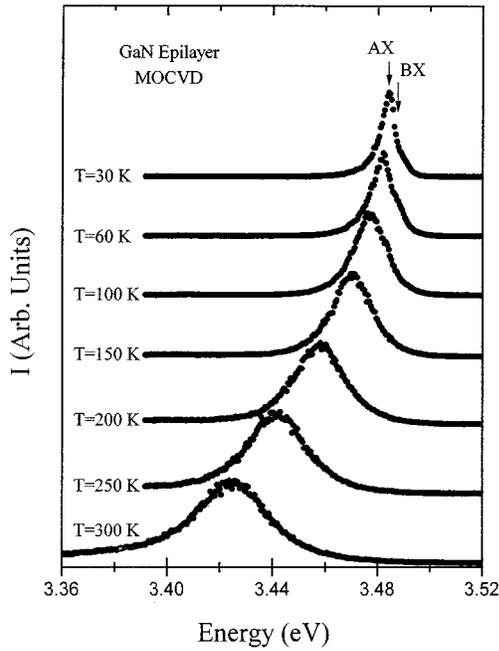[a]Electronic mail: jiang@phys.ksu.edu

FIG. 1. cw PL spectra of a MOCVD grown high quality and purity GaN epilayer measured at different temperatures. The arrows at 30 K spectrum indicate the peak positions of the ground states of the A- and B-exciton transitions.

FIG. 2. cw PL spectra measured at $T=300$ K for several representative I_{exc}. The solid lines near the PL maxima are the least-squares fit of data using the Gaussian functions and the arrows indicate the fitted peak positions.

about 20 meV,[3–5] the broad linewidth however makes it impossible to determine the origin of the PL emission at RT as shown in Fig. 1.

For the band-to-band transition, the peak position of the emission line would shift toward lower energies with increasing excitation intensity, I_{exc}, due to the enhanced many body and screening effects of free carriers.[10] The first order exchange energy due to the many body effect of the free electrons and holes using the Thoma-Fermi screening potential is given by[10]

$$\Delta E_g|_{exch} = (-2e^2 k_F / \pi \epsilon)[1 + (\pi \kappa / 2k_F)$$
$$- (\kappa / k_F)\tan^{-1}(k_F / \kappa)]. \quad (1)$$

Here κ is the reciprocal screening length[11] and k_F the Fermi wave vector:

$$\kappa = 2.73 \times 10^4 (m_e/m_0)^{1/2}(n^{1/6}/\epsilon^{1/2}) \text{ cm}^{-1}, \quad (2)$$

$$k_F = 3.094 n^{1/3} \text{ cm}^{-1}, \quad (3)$$

where $m_e(m_0)$ is the electron effective (free) mass, ϵ is the dielectric constant, n is the free-carrier concentration. From Eqs. (1) to (3), if $\kappa/k_F \ll 1$ (or for relatively large values of n), we have,

$$\Delta E_g|_{exch} = (-2e^2 k_F / \pi \epsilon) \propto -k_F \propto -n^{1/3} \propto -I_{exc}^{1/3}. \quad (4)$$

The last step in Eq. (4) is based on the fact that n is proportional to I_{exc}, $n \propto I_{exc}$. We thus obtain for the band-to-band transition an expression for the PL emission peak position

$$E = E_g(n \to 0) + \Delta E_g|_{exch} = E_g(n \to 0) - \alpha I_{exc}^{1/3}, \quad (5)$$

where α is a proportionality constant.

Figure 2 shows PL spectra of a GaN epilayer measured at RT for four different excitation intensities. We have fitted PL spectra near the emission peaks by the Gaussian func-
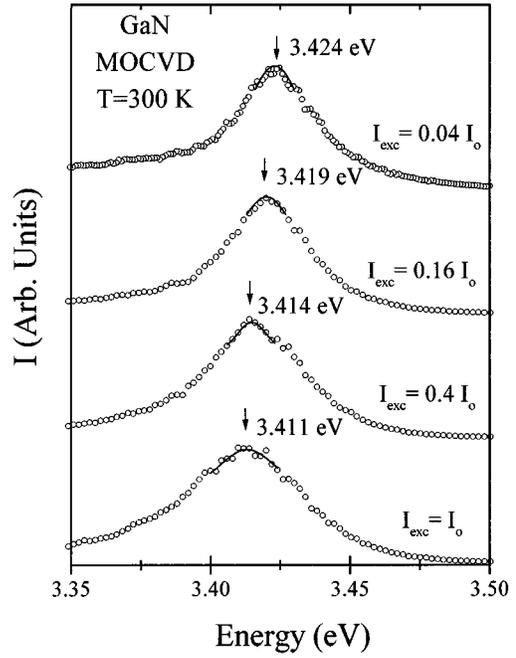
tions to accurately determine the peak positions. The arrows indicate the peak positions of the PL spectra. It is clear that the emission peak position shifts toward lower energies with increasing I_{exc}. In Fig. 3, we plotted the peak position E_p, of the PL emission line as a function of $(I_{exc})^{1/3}$. It clearly shows a linear relation between E_p and $(I_{exc})^{1/3}$ and is a direct evidence for the band-to-band transition.[10,12] The solid line in Fig. 3 is the least-squares fit of data with Eq. (5) and
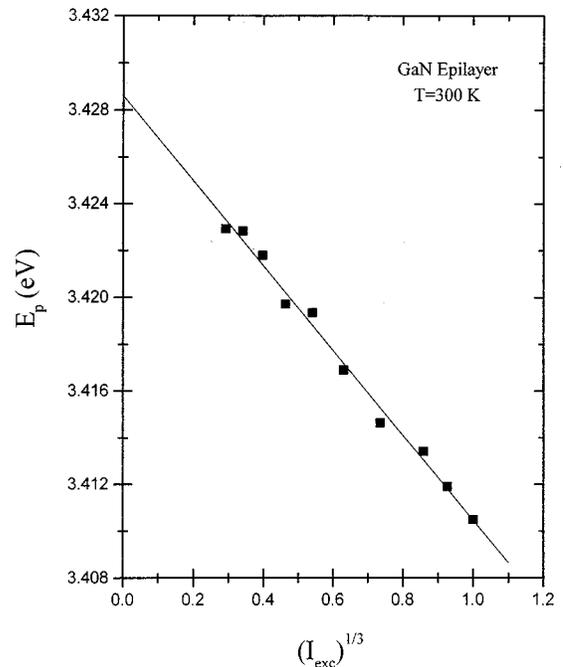

FIG. 3. The spectral peak positions of the PL emission line at RT, E_p vs $(I_{exc})^{1/3}$. The solid line is the least-squares fit of data with Eq. (5).
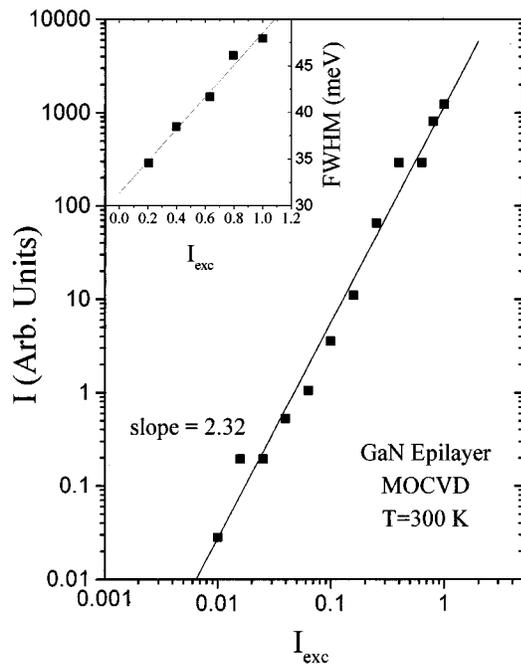
FIG. 4. I_{exc} dependence of the total emission intensity. The solid line is the least-squares fit of data with Eq. (6). The inset is the I_{exc} dependence of the full width at half-maximum of the RT PL emission line, where the solid line is a linear fit of data.

the fitted value of $E_p(0) = 3.429$ eV corresponds to the band-to-band transition energy at the limit of a single pair of electron and hole at RT. Since Eq. (5) is not expected for an excitonic transition, it thus indicates that the band-to-band transition is the dominant optical transition at RT in high quality and purity MOCVD grown GaN epilayers.

In Fig. 4, we plotted the I_{exc} dependence of the emission intensity, I_{emi}, at RT. I_{emi} depends on I_{exc} superlinearly following

$$I_{emi} \propto I_{exc}^{\beta}. \qquad (6)$$

The linear line in Fig. 4 is the least-squares fit of data with Eq. (6) and the fitted exponent $\beta = 2.32$, which is again consistent with the assignment of the band-to-band transition. The inset of Fig. 4 plots the I_{exc} dependence of the full width at half-maximum (FWHM) of the PL emission line at RT and reveals that FWHM also increases linearly with I_{exc} as indicated by the solid line. The increase of FWHM with I_{exc} is also expected for the band-to-band transition since increasing I_{exc} would increase the energy distribution of the electrons and holes and hence the linewidth.

We have also calculated the thermal equilibrium distribution of the free electron and hole versus exciton concentration at RT,[13] which is consistent with our experimental results reported here. Under thermal equilibrium at RT, our calculations indicate that the free-carrier concentration is higher than that of the bound states (free excitons) and that the exact free carrier and exciton concentrations depend on the total carrier concentration. Here, the calculation result together with experimental observation points to several important consequences. First, the radiative recombination rate of the band-to-band transition in GaN cannot be very small at RT and should be comparable with that of the exciton

transition since the total transition probability of the band-to-band transition depends not only on the total free-carrier concentration but also on its radiative recombination rate. Second, the band-to-band transition at RT observed here is consistent with the fact that GaN crystalline quality and purity are still not as high as those of other conventional III–V semiconductors, say GaAs. It has been indicated that the band-to-band transition becomes more probable at higher temperatures and also in less pure or less perfect crystals, where local field tends to break up the exciton into free carriers.[14] Third, the fact that the band-to-band transition is the dominant transition at RT indicates that the free electron and hole recombination is very important for device applications, including blue LEDs and LDs. For example, the possibility of exciton molecules being responsible for the laser emission can certainly be precluded in GaN LDs. Fourth, excitons can still be formed at RT,[15] but the important fact is that the exciton transition is not the dominant transition at RT in MOCVD grown GaN epilayers. For different materials and structures, the dominant intrinsic optical transitions at RT could be modified. Detailed studies are in progress.

In summary, PL emission properties have been investigated for high quality and purity MOCVD grown GaN epilayers to understand the mechanisms of optical transitions at RT. By varying excitation intensity, I_{exc}, it is found that the emission spectral peak position, E_p, shifts toward the lower energies following the expression $E_p \sim I_{exc}^{1/3}$. Together with the I_{exc} dependencies of the PL emission intensity and FWHM, we conclude that the band-to-band transition is the dominant optical transition in MOCVD grown GaN at RT. It thus should also be one of the most important transitions for many device applications using GaN.

[1] H. Morkoç, S. Strite, G. B. Gao, M. E. Lin, B. Sverdlov, and M. Burns, J. Appl. Phys. **76**, 1363 (1993).
[2] H. Morkoç and V. N. Mohammad, Science **267**, 51 (1995).
[3] 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); M. Smith, J. Y. Lin, H. X. Jiang, A. Salvador, A. Botchkarev, W. Kim, and H. Morkoç, Appl. Phys. Lett. **69**, 2453 (1996).
[4] G. D. Chen, M. Smith, J. Y. Lin, H. X. Jiang, S.-H. Wei, M. Asif Khan, and C. J. Sun, Appl. Phys. Lett. **68**, 2784 (1996).
[5] D. C. Reynolds, D. C. Look, W. Kim, A. Özgür, A. Botchkarev, A. Salvador, H. Morkoç, and D. N. Talwar, J. Appl. Phys. **80**, 594 (1996).
[6] W. Shan, T. J. Schmidt, R. J. Haustein, J. J. Song, and B. Goldenberg, Appl. Phys. Lett. **66**, 3492 (1995).
[7] C. I. Harris, B. Monemar, H. Amano, and I. Akasaki, Appl. Phys. Lett. **67**, 840 (1995).
[8] A. Salvador, G. Liu, W. Kim, Ö. Aktas, A. Botchkarev, and H. Morkoç, Appl. Phys. Lett. **67**, 3322 (1995).
[9] J. Ding, M. Hagerott, T. Ishihara, H. Jeon, and A. V. Nurmikko, Phys. Rev. B **47**, 10528 (1993).
[10] R. A. Abram, G. J. Rees, and B. L. H. Wilson, Adv. Phys. **27**, 799 (1978).
[11] E. X. Ping and H. X. Jiang, Phys. Rev. B **47**, 2101 (1993).
[12] D. C. Reynolds (private communication).
[13] Z. Shou, J. Y. Lin, and H. X. Jiang (unpublished).
[14] J. I. Pankove, *Optical Processes in Semiconductors* (Dover, New York, 1971), Chap. 6.
[15] W. Shan, T. J. Schmidt, S. Bidnyk, A. J. Fischer, B. D. Lettle, and J. J. Song, Fourth Wide Band Gap and Nitride Workshop, St. Louis, 1997.