

# Effect of temperature on longitudinal optical phonon-assisted exciton luminescence in heteroepitaxial GaN layer

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First-order and second-order longitudinal optical (LO) phonon-assisted luminescence lines of neutral donor-bound excitons and free excitons in heteroepitaxial GaN film have been investigated in temperature range from 3.5 to 50 K. The energy spacing between the exciton resonant lines and their corresponding LO phonon replicas is found to be strong temperature dependent. Permogorov's theory on LO phonon-assisted luminescence of free excitons could be employed to explain the main experiments. It is also found that the interaction strength of the free exciton with LO phonon is stronger than that of the bound exciton with LO phonon. © 2000 American Institute of Physics. [S0003-6951(00)04047-X]

The shallow neutral donor-bound exciton emission (usually noted as  $D^0$ ,  $X$ , or  $I_2$ ) often dominates in low-temperature photoluminescence spectrum of heteroepitaxial GaN films. Currently, the highest quality heteroepitaxial GaN films grown by metalorganic vapor phase epitaxy (MOVPE) have  $D_0$ ,  $X$  linewidths between 2 and 3 meV at low temperature.<sup>1</sup> In the heteroepitaxial thick GaN films grown by hydride vapor phase epitaxy (HVPE) the neutral donor-bound exciton linewidths are as narrow as about one unit electron volt. As a result, a rich variety of fine structure is resolved, for example, two or more neutral donor-bound exciton transitions have been identified.<sup>1,2</sup> On the other hand, as a polar semiconductor, exciton-longitudinal optical (LO) phonon coupling in GaN is strong enough to permit that the phonon-assisted exciton luminescence lines can be observed.<sup>3-6</sup> In the literature<sup>3-5</sup> the LO phonon-assisted free-exciton luminescence in the epitaxial GaN films has been investigated. Reynolds *et al.*<sup>6</sup> observed the phonon sidebands of the donor-bound exciton transition in the relatively thick GaN epilayers grown by HVPE. In this letter, we present the first-order and second-order LO phonon-assisted luminescence lines of the neutral donor-bound excitons and the free excitons in the heteroepitaxial GaN film at different temperatures from 3.5 to 50 K. It is found that the energy separations between the phonon sidebands and their principle lines exhibit unusual temperature dependence. Moreover, the two-phonon energy spacing shows a significantly smaller decrease with temperature from 3.5 to 50 K than the one-phonon energy spacing.

The sample used in the experiment was grown on  $c$  plane of sapphire by MOVPE. A 2.88  $\mu\text{m}$  GaN layer was grown followed a 40 nm GaN nucleation layer. The sample is nominally undoped. In the photoluminescence (PL) measurements, the sample was mounted on the cold finger of a Janis closed cycle cryostat with varying temperature from

3.5 to 300 K, and excited by the 325 nm line of a Kimmon He-Cd continuous wave laser with output power of 40 mW. The emission signal was dispersed by a SPEX 750M monochromator and detected with a Hamamatsu R928 photomultiplier. The lock-in amplifier technology was not used because of strong enough emission signal.

The exciton PL spectra of the sample at different temperatures are shown in Fig. 1. Clearly, the neutral donor-bound exciton ( $D^0, X$ ) line dominates in the examined low-temperature range. Its linewidth is 2.4 meV under low power excitation, indicating high quality of the sample. In strain-relaxed GaN samples (homoepitaxial films,<sup>7</sup> or thick heteroepitaxial films)<sup>2,8</sup> the  $D^0, X$  peak occurs at 3.471 eV at low temperature. In our sample, the  $D^0, X$  peak is at 3.490 eV at 4 K, indicating a large compressive, biaxial stress, which we estimate to be 1.2 GPa. The free exciton A transition (FXA) is also well resolved. Besides the  $D^0, X$  peak and FXA transition, one pair of weaker peaks with energy  $\sim 20$  meV lower

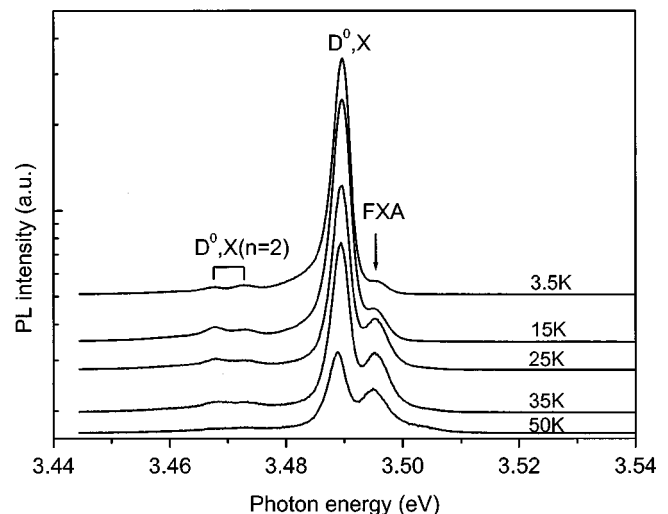


FIG. 1. The exciton resonant luminescence spectra of the GaN epilayer at different temperatures.

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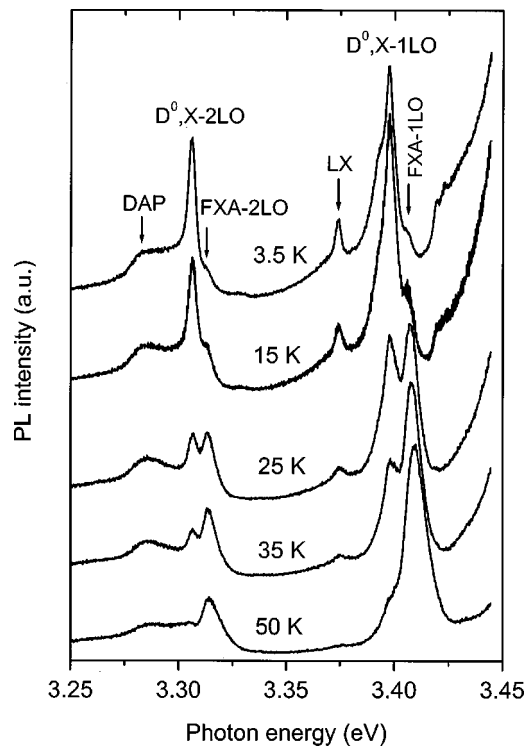


FIG. 2. The LO phonon-assisted luminescence spectra measured at different temperatures.

than that of the  $D^0, X$  line are observed. They have been recently identified to be the excited state transitions [denoted by  $D^0, X$  ( $n=2$ )] of the  $D^0, X$  using magnetospectroscopy technique by Skromme *et al.*<sup>2,9,10</sup> Actually, existence of the large number of excited states is an important feature of the shallow donor-bound excitons in direct gap III-V and II-VI compound semiconductors.<sup>11</sup>

As temperature increases, the relative intensity of the FXA line with respect to the  $D^0, X$  line rapidly increases. This is obviously due to thermal dissociation of the bound excitons into the free excitons.<sup>3</sup> However,  $D^0, X$  transition still keeps its dominant position in the interested temperature range. The relative intensity of the phonon sidebands of the FXA with respect to the phonon sidebands of the  $D^0, X$  increases with temperature more significantly than that of the FXA with respect to the  $D^0, X$ , as shown in Fig. 2. At about 25 K, the phonon sidebands of the FXA already become dominant. When the temperature is further increased to 50 K, the phonon sidebands of the  $D^0, X$  almost disappears. These facts imply that the coupling strength of bound exciton with LO phonon is much weaker than that of free exciton with LO phonon. Relatively broad peak denoted by DAP is the distinct donor-acceptor pair recombination.<sup>12</sup> Another excitonic transition (LX) may be from the radiative recombination of the excitons localized at extended defects in the GaN.<sup>1,13,14</sup>

It is known that the LO phonon characteristics energy can be determined from the energy spacing between the exciton resonant lines and their LO phonon sidebands.<sup>6</sup> It comes as a surprise that the energy spacing exhibits an unusual temperature dependence, as shown in Fig. 3. The characteristic energy of  $A_1$ -LO phonon of GaN has been determined to be  $\sim 92$  meV with low-temperature PL technique.<sup>3-6</sup> Thus, the dot lines at 92 meV are used as ref-

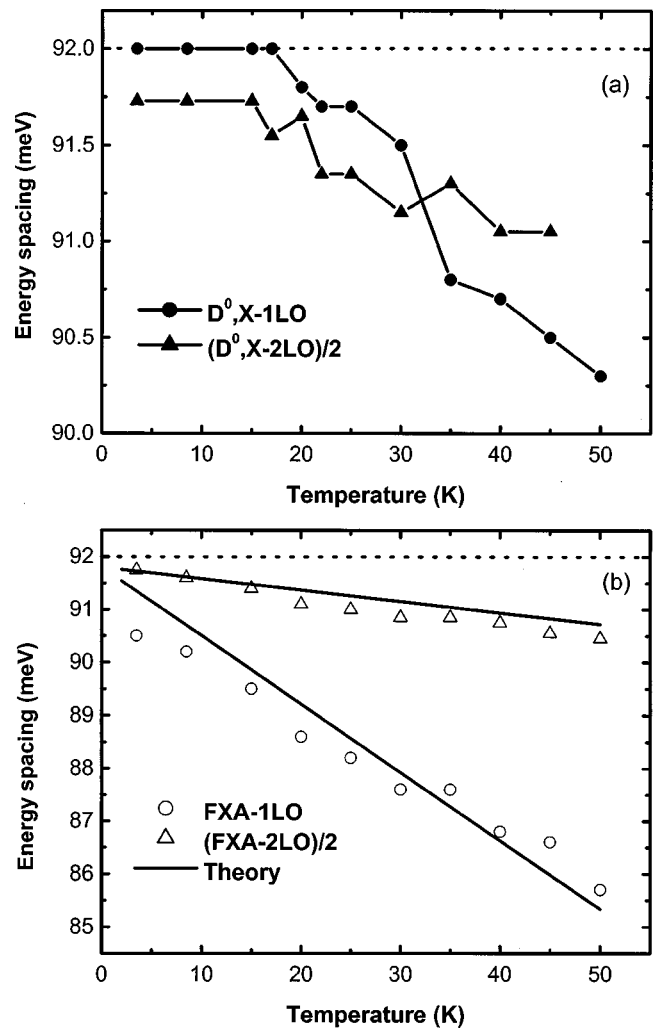


FIG. 3. The 1LO phonon energy spacing and 2 LO phonon energy spacing versus temperature, (a) determined from donor-bound exciton transitions; (b) determined from free exciton transitions. The solid lines in (a) are guide to eye while the solid lines are the theoretical results in (b). The dot lines at 92 meV in (a) and (b) are plotted as reference lines.

ference lines in Fig. 3. Four physical quantities, denoted by  $D^0, X-1LO$ ,  $(D^0, X-2LO)/2$ ,  $FXA-1LO$ , and  $(FXA-2LO)/2$ , respectively, were plotted as a function of temperature in Fig. 3. Both the  $D^0, X-1LO$  and the  $FXA-1LO$  exhibit a surprising decrease with temperature. Compared with the  $D^0, X-1LO$  and the  $FXA-1LO$ , however, the  $(D^0, X-2LO)/2$  and  $(FXA-2LO)/2$  show much weaker temperature dependence. Generally, for the sample investigated here, there are three possible physical mechanisms that can cause shift of the energy separations with temperature. The first factor is lattice thermal expansion due to vibrational anharmonicity of solid atoms or molecules. It is expected that the phonon energy decreases with increasing temperature. Following Liu *et al.*'s work<sup>15</sup> on the temperature dependence of the LO phonons of the GaN films, we calculate the shift amount of the  $A_1$ -LO phonon frequency of the GaN film for temperature varying from 4 to 50 K using the Cui's empirical formula.<sup>16</sup> The shift is found to be only  $0.002 \text{ cm}^{-1}$  when the parameters obtained by Liu *et al.*<sup>15</sup> were adopted in calculation. Debernardi's first principles calculations<sup>17</sup> also show a very small shift of the phonon frequency due to anharmonic effect in the interested tem-

perature range. Therefore, the thermal expansion should be ruled out as a main factor causing the observable large temperature dependence of the phonon energy in the GaN film.

Another factor causing a shift of the phonon frequency is pressure or stress.<sup>18</sup> As mentioned earlier, the residual stress in the GaN film investigated in the present work is estimated to be 1.2 GPa. Such a large residual stress is mainly due to the thermal expansion coefficient difference between GaN epilayer and sapphire substrate.<sup>8</sup> It should be expected that the change in the thermal stress and thus the change in the optical phonon frequency is negligibly small in the temperature range from 4 to 50 K although the low-temperature thermal coefficients of GaN are not available so far.<sup>19,20</sup>

The third factor should be from the exciton-phonon coupling mechanism. According to Permogorov's theory<sup>21</sup> on optical emission due to free exciton scattering by LO phonons in semiconductors, the spectral shape of the phonon-assisted luminescence lines can be described by the general formula

$$J_N(\varepsilon) = \varepsilon^{1/2} \exp(-\varepsilon/k_B T) W_N(\varepsilon), \quad (1)$$

where  $W_N(\varepsilon)$  is the probability of the  $N$ th order phonon-assisted annihilation for the exciton with the kinetic energy  $\varepsilon$ . The spectral lineshape defined by Eq. (1) is a typical asymmetrical lineshape. If  $W_N$  is a simple power function of the excitonic kinetic energy  $W_N \propto \varepsilon^L$ , the halfwidth of Eq. (1) depends linearly on temperature with a slope unambiguously related to the exponent  $L$ . The more interesting theoretical prediction is that the shift  $\Delta$  of the line maximum from its low-energy threshold ( $\varepsilon=0$ ) also increases linearly with temperature

$$\Delta = (L + \frac{1}{2})k_B T. \quad (2)$$

The shift of the line maximum of phonon-assisted luminescence lines with temperature will doubtless result in reduction of the energy spacing between the zero-phonon line and its phonon replica line. The reduction speed of the energy spacing depends obviously on the exponent  $L$ . For the case of 1LO phonon scattering, Permogorov theoretically demonstrated that the probability  $W_1$  is approximately proportional to the kinetic energy  $\varepsilon$ . In other words,  $L=1$  for the first-order LO phonon-assisted luminescence. For the second-order LO phonon-assisted luminescence, it has been found that the annihilation probability is independent of the excitonic kinetic energy, that is,  $L=0$ . According to earlier analysis, the 1LO energy spacing will linearly decrease with temperature in a slope of  $-\frac{3}{2}k_B$ . The 2LO energy spacing defined in the present work will also linearly decrease with temperature but in a much smaller slope of  $-\frac{1}{4}k_B$ . The solid lines in Fig. 3(b) are the theoretical results based on the Permogorov's model. In the theoretical calculations, the characteristic energy of  $A_1$ -LO phonons at 0 K was taken as 91.8 meV. The agreement between the experiments of free excitons and the theory is very well. However, the temperature of the  $D^0, X$ -1LO is much weaker than that of the FXA-1LO. The change of the  $D^0, X$ -1LO in the examined temperature range is only 1.7 meV/92 meV  $\approx$  1.8% while the change of the FXA-1LO is 6.3 meV/92 meV  $\approx$  6.8%. This indicates that there is a significant difference in scattering

mechanism between free exciton-phonon and bound exciton-phonon. Together with the much stronger temperature dependence of the emission intensity of the 1LO phonon-assisted luminescence line, the much weaker temperature dependence of the  $D^0, X$ -1LO indicates that the coupling strength of the bound excitons with the LO phonons is much smaller than that of the free excitons.

In summary, the LO phonon-assisted luminescence of the shallow donor-bound excitons and free excitons in the heteroepitaxial GaN film has been investigated at different temperatures. Anomalous temperature dependence of the energy separation between the principal exciton resonant lines and their responding phonon replicas was found. Moreover, 1LO phonon spacing exhibits much stronger temperature dependence than 2LO phonon spacing does. It was found that the Permogorov's theory could be employed to interpret our main experiments.

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