

Free exciton emission in GaN

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We present a detailed study of the free exciton emission in GaN. Photoluminescence and photoluminescence excitation techniques are employed to show the dominant role of exciton-phonon interaction in the creation of the free exciton states and the free exciton emission cascade in GaN. Up to six longitudinal optical (LO) phonon replicas are observed in both photoluminescence and photoluminescence excitation spectra. From an analysis of the free exciton line shape we are able to conclude that free exciton emission and the interaction of free excitons with LO phonons have to be described within the framework of the momentum conservation law. The exciton kinetic energy distribution is found to be a Maxwellian one having the temperature of the lattice. This suggests an enhanced rate of free exciton scattering on the acoustic phonons, in contrast to other wurzite-type semiconductors. [S0163-1829(96)01428-2]

I. INTRODUCTION

GaN with the wurzite-type crystal structure is a direct band gap semiconductor. Since the first report¹ on its optical properties, numerous investigations have been made because of promising optoelectronic applications of this material. Most of the works have reported on donor and acceptor bound exciton emission,¹⁻³ shallow donor-acceptor pair recombination,^{1,4} and the observation of the deep yellow band emission.¹ Free *A*, *B*, and *C* exciton states have been identified mainly in photoluminescence excitation⁵ and reflection measurements,¹ whereas they have rarely been observed in photoluminescence.⁶

To the best of our knowledge up to now there is no information concerning the kinetic properties of free excitons (FE's) such as exciton formation under optical excitation and its relaxation to the thermal equilibrium state. One of the principal features of the optical processes related to the FE's in the polar semiconductors is the intensive interaction with LO phonons regarded as Fröhlich polar intraband scattering.⁷ This effect to a large extent determines the FE recombination and kinetic energy relaxation within the exciton band. These phenomena have been widely studied in a variety of polar semiconductors: CdS,⁸⁻¹⁰ ZnSe,¹¹ CdSe,¹² and others.

In this paper we first describe the exciton emission processes due to zero-phonon and multiphonon transitions. The important feature of the phonon-assisted FE emission lines is that their shapes reflect the exciton kinetic energy distribution. Second, we discuss the mechanism of the formation of FE states and the processes responsible for the kinetic energy relaxation of the hot excitons in GaN.

II. EXPERIMENT

Hexagonal GaN films are prepared by hydride and organometallic vapor phase epitaxy on sapphire or 6H-SiC with the *c* axis perpendicular to the surface plane. Photoluminescence (PL) is excited by the 3.8 eV line of a He-Cd cw laser

and detected with a single monochromator using standard lock-in technique. The spectral resolution is better than 0.2 Å. The exciting light is polarized perpendicular to the hexagonal axis of the crystals. All PL spectra are corrected for the spectral sensitivity of the detection system. The photoluminescence excitation (PLE) technique has been employed to monitor the resonant excitation of the FE transitions. The light from a 1000 W Xe arc lamp is dispersed by a single monochromator with the spectral width of 3 Å and focused onto the sample using quartz lens optics. The emission is collected with a quartz lens condenser as well and spectrally resolved with a second single monochromator. The intensity of the emitted light is normalized simultaneously with respect to the intensity of the exciting radiation by inserting a quartz beam splitter in the path of the exciting light. A pyrodetector with a constant spectral sensitivity is used to measure the flux of the exciting light. PL and PLE measurements are performed in the temperature range of 1.5 to 300 K.

III. RESULTS

A. Free exciton luminescence

The emission of the exciton bound to the neutral donors dominates in the PL spectra measured in the temperature region from 2 to 30 K. Because of its small localization and, hence, activation energy, an increase of the temperature leads to an efficient quenching of the bound exciton line. The full width at half maximum of the bound exciton line is 5 meV at $T=2$ K. Therefore, to avoid problems with overlapping of luminescence lines, the major parts of the experiments are done in the temperature interval from 50 to 100 K. At these temperatures, lines related to the annihilation of the FE states become dominating in the PL spectra.

The emission spectrum of free excitons in GaN is shown in Fig. 1. The oscillatory structure of the spectrum has an apparent 92 meV energy periodicity [LO-phonon energy of GaN (Ref. 13)] with respect to the zero-phonon exciton transition. We marked on this figure LO-phonon positions with

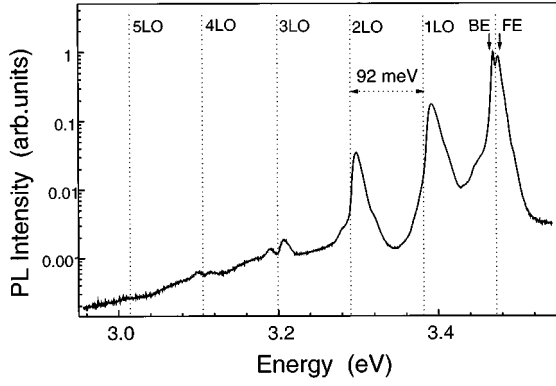


FIG. 1. Photoluminescence spectrum of GaN on SiC at $T=50$ K on a logarithmic scale. In addition to resonant emission lines of free (FE) and bound excitons (BE) indicated by arrows, up to 5LO-phonon replicas of the FE are observed. Vertical grids indicate the energy positions of LO phonons with respect to the bottom of the FE band.

respect to the energy of the bottom of the exciton band, since the shapes of the FE-related emission lines are different. As follows from our experiments, the ratio between phonon replica intensities does not depend on the type of the substrate used for the growth of the GaN epitaxial layer. The ratio of the zero-phonon line integral intensity to one-phonon and two-phonon lines is 14:2.5:1, while a significant drop of the intensity can be easily seen for the higher order phonon-assisted FE transitions. We would like to point out that a similar behavior has been observed for the bound exciton emission and donor-acceptor pair recombination in a variety of polar semiconductors. The evidence identifying it with the FE transitions can be drawn from the analysis of the line shapes of zero-phonon and phonon-assisted FE transitions.

One of the main properties of free excitons is its ability to move in the crystal. As a result, the kinetic energy of excitons spreads over some \vec{k} values. From the momentum conservation law, only excitons with a wave vector close to the small wave vector of the photons are allowed to recombine radiatively. The exact shape of the zero-phonon line has to be, strictly speaking, described in the framework of the free exciton polariton approach.¹⁴ However, certain conclusions can be drawn from the simple consideration of the temperature dependence of the shapes of the zero-phonon and phonon-assisted FE emission lines.

The inset of Fig. 2 depicts the temperature dependence of the integral intensity of the FE emission line. The FE thermal activation energy is found to be 26.7 ± 0.3 meV. This value is in excellent agreement with the spectral position of the FE line with respect to the band gap edge.^{5,15} We would like to mention that the thermal activation slope is deduced in the temperature region where the influence of the bound exciton line is negligible due to its small thermal activation energy (see Fig. 2). The preexponential factor C in the Arrhenius plot $I(T) = I(T=0) / [1 + C \exp(-E_{FE}/kT)]$ where $E_{FE} = 26.7$ meV is rather large: $C = 620$. If we neglect the bound exciton transitions and consider only the contribution from the A valence band, at high enough temperatures this number represents the ratio between the rates of nonradiative and radiative transitions in which free $e-h$ pairs and FE's are competing. Thus, this number indicates a rather poor quan-

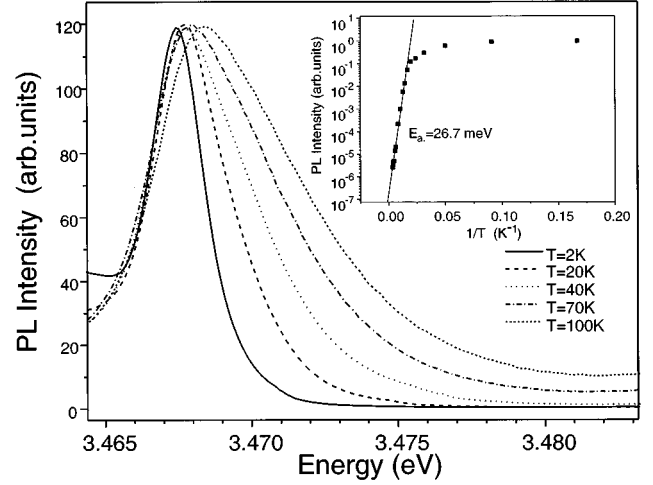


FIG. 2. FE zero-phonon line shape at different temperatures. Inset: Arrhenius plot of the integrated intensity of the FE line. The analysis gives a FE activation energy of $E_{FE} = 26.7 \pm 0.3$ meV coinciding with the optical position of this line with respect to the band gap.

tum yield for the FE transitions in our samples. This result is in good agreement with the FE effective lifetime measurements.¹⁶ At elevated temperatures the observed FE lifetimes are in the range of 10 ps and, obviously, determined by nonradiative processes. From the prefactor $C = 620$ an estimate for the FE radiative lifetime gives $\tau = 6-8$ ns, which is of the order of the FE radiative lifetime in high quality CdS crystals.¹⁷

Figure 2 exhibits a set of PL spectra of the zero-phonon line measured at different temperatures. The energy scale of these curves has been shifted in order to compensate for the variation of the band gap with temperature. The characteristic feature of these lines is an abrupt cut of the Stokes part of the line and a temperature broadening of the anti-Stokes one. This is the classical behavior expected for the FE line. Bound electron states usually demonstrate either a symmetrical broadening of the line or an asymmetrical one, more pronounced in the Stokes part of the spectrum depending on the mechanism of electron-phonon coupling.

The observed tendency at the red edge of the line can be easily explained taking into account the very low density of exciton states in the vicinity of the polariton bottleneck. In addition, the process of kinetic energy relaxation of FE's into this region via emission of long wavelength acoustic phonons is inefficient considering the FE lifetimes. The high energy part represents the thermal distribution of the kinetic energies of the excitons in the band. However, as we mentioned above, the recombination of excitons with $k_{ex} > 0$ is forbidden due to the \vec{k} conservation law. Therefore the interaction with acoustic phonons or inelastic scattering by impurities or by other defects has to be taken into consideration. The probability of exciton interaction with acoustic phonons is proportional to a form factor¹⁸⁻²⁰

$$P(q) \propto \frac{q}{[1 + (1/2\beta a_B q)^2]^4}. \quad (1)$$

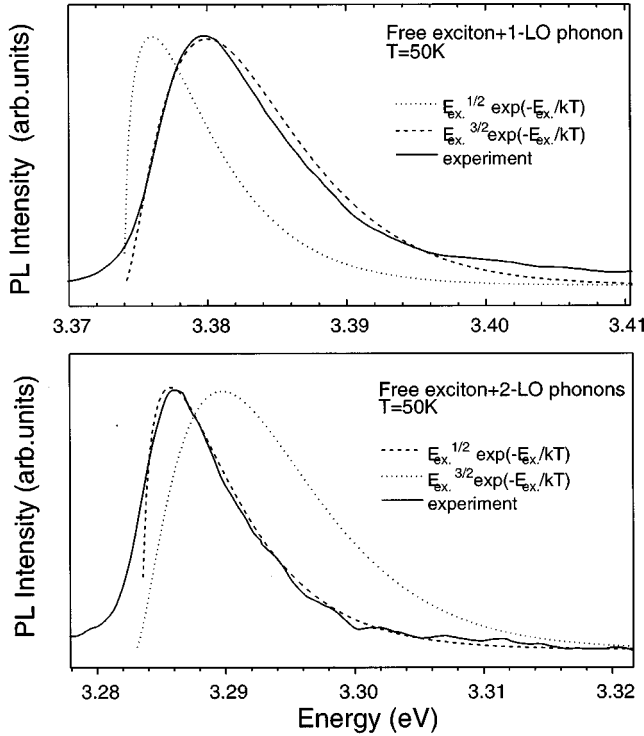


FIG. 3. High temperature 1LO FE and 2LO FE replica line shapes (solid lines). Dashed and dotted lines represent calculated shapes of these lines as stated in the text ($T=50$ K).

Here $\beta = m_h/2(m_e + m_h)$, $q = E_{ph}/\hbar S$ is the phonon wave vector (S is the velocity of sound), and $a_B = \sqrt{\hbar^2/2\mu E_{ex}}$ (μ is the reduced mass) is the Bohr radius of exciton. Substituting the values $E_{ex} = 26.7$ meV, already at the energy of the phonon $E_{ph} = 10$ meV we obtain $1/2(\beta q a_B) > 1$. The factor $1/2(\beta q a_B)$ rapidly lowers the probability of interaction with high energy acoustic phonons. It is the reason why a thermal equilibrium distribution within the zero-phonon line has not been observed in our experiments. From the momentum conservation law it can be shown that phonons with $q = k_{ex}$ mainly interact with FE's,¹⁸ so excitons in the vicinity of the bottom of the band (with kinetic energy of the order of 1 meV for k_{ex} in the range of 10^6 cm⁻¹) can emit only low energy phonons. Therefore the fast decrease of the PL intensity in the vicinity of the polariton bottleneck is determined mainly by the low density of the exciton states.

The main consequence of the LO-phonon participation in the recombination of FE's is a breakdown of the momentum conservation law. Indeed, excitons with any k_{ex} are allowed to recombine, transferring the momentum to the phonon. Because of a small energy dispersion of the LO-phonon branch the shape of the phonon-assisted FE recombination lines reflects the kinetic energy distribution in the exciton gas. Figure 3 shows spectra of the one-LO- and two-LO-phonon replicas of the FE emission. The shape of the two-LO-phonon replica can be fitted with good accuracy by a Maxwell distribution having the temperature of the lattice:

$$I(E_{ex}) \propto E_{ex}^{1/2} [\exp(-E_{KE}/kT)] \quad (2)$$

where $E_{ex}^{1/2}$ is the density of states in a parabolic exciton band in a direct band gap semiconductor, E_{KE} is the exciton ki-

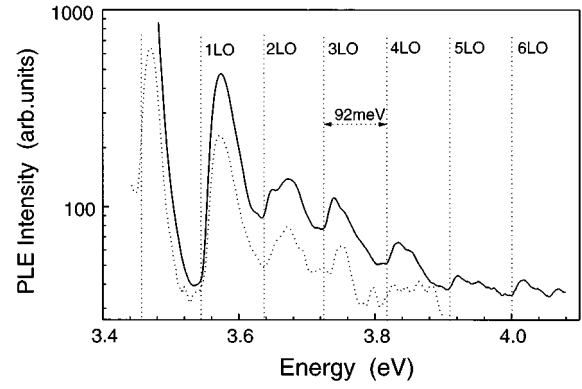


FIG. 4. Photoluminescence excitation spectra of the zero-phonon FE line (solid line) and 1LO FE replica (dotted line) at $T=70$ K.

netic energy (scaled with respect to the bottom of the exciton band), and T is the temperature of the lattice. Note that both E_{ex} and E_{KE} have the same values. The contour of the 1LO replica is found to be described by the function

$$I(E_{ex}) \propto E_{KE} E_{ex}^{1/2} [\exp(-E_{KE}/kT)]. \quad (3)$$

Here the additional prefactor E_{KE} represents the probability of phonon-assisted recombination of the exciton with kinetic energy E_{KE} . For the two-phonon process this probability is independent of the exciton kinetic energy. The fits using Eqs. (2) and (3) can be done successfully over a wide temperature range for both lines, demonstrating that the FE subsystem is in thermal equilibrium with the lattice.¹⁰

B. Free exciton excitation spectra

The free exciton state can result from the binding of free electron-hole pairs photogenerated via the absorption continuum or by an indirect phonon-assisted exciton formation. The most developed tool to distinguish between these processes is the study of the FE excitation spectrum.⁹⁻¹¹ Due to the momentum and energy conservation rules, every point of the FE emission lines is related to some special point in the exciton band. Therefore the exciton resonances induced by indirect exciton absorption with the simultaneous creation of a free exciton and some LO phonons, or followed by a LO-phonon cascade in the exciton band, can be monitored. These processes determine the kinetics of FE's, and they cannot be seen in absorption spectra. Figure 4 exhibits the PLE spectra detected at the energy of the FE zero-phonon and the 1LO-phonon-assisted emission lines. For the zero-phonon line up to six resonant features with apparent 92 meV periodicity are seen. As already mentioned above, we have to mark the LO-phonon positions with respect to the bottom of the FE band. For the 1LO-phonon replica the resonance due to the direct FE excitation is detected as well. The intensities of these PLE peaks and their line shapes slightly vary for different samples (the spectral position of FE lines might differ from sample to sample due to the strain in the GaN layers, i.e., thermal mismatch between layers and substrates¹⁵). Despite this fact, their spectral positions with respect to the zero-phonon FE line and all general features are exactly the same. The spacing precisely corresponds to the LO-phonon energy,

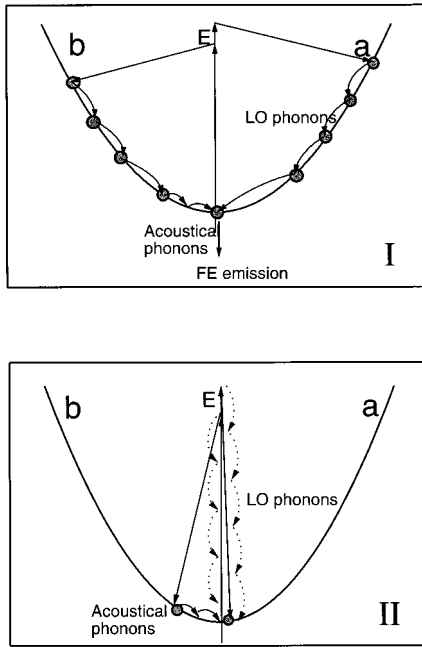


FIG. 5. Schematic representation of two possible mechanisms of the creation of the free exciton emitting state (near to the bottom of the FE band). (I) “Hot exciton” cascade; (II) creation of the low energy exciton with simultaneous emission of few LO phonons. Excitation energy coincides (curve *a*) and does not coincide (curve *b*) with nE_{LO} .

rather than to $E_{LO}(1+m_e/m_h)$, where m_e and m_h are the electron and hole effective masses. This is a strong indication for an indirect phonon-assisted excitation of the FE rather than formation of electrons and holes with subsequent relaxation via phonon emission.

The amplitude of the phonon-related oscillations rapidly decreases toward higher energies and the intensity of the background is nearly an order of magnitude lower. This suggests that the probability of FE creation due to interband $e-h$ transitions is much lower than the indirect FE excitation. The resonance features in the PLE spectra were explained in the framework of a hot exciton cascade⁹ [Fig. 5(I)]. In a first step, the absorption of a single quantum leads to the creation of a FE with high kinetic energy and one LO phonon (to accomplish k conservation). The following FE energy relaxation down to the bottom of the exciton band is caused by the FE scattering on LO phonons through the intermediate states in the exciton band. If the energy of the initial state differs by nE_{LO} (where n is an integer and E_{LO} is the LO-phonon energy) with respect to the bottom of the exciton band, the thermalization process is completed within 10^{-13} – 10^{-12} s, the typical time for the interaction with LO phonons [Fig. 5(I), curve *a*]. In the opposite case scattering with acoustic phonons is required for the FE to reach the thermal equilibrium with the lattice [Fig. 5(I), curve *b*].

For the majority of polar semiconductors the FE binding energy is of the order of the LO-phonon energy. The main difference from GaN is that the energy of the LO phonon is approximately four times larger than the FE binding energy. From a similar investigation on A_2B_6 compound semiconductors,⁹ the existence of FE’s with a kinetic energy

as high as 0.2 eV has been postulated. Since up to six phonon replicas can be seen in the PLE spectrum of GaN, one can raise the question as to whether free excitons with kinetic energies up to 0.46 eV exist. To our mind, since the annihilation of FE’s with the simultaneous emission of a few LO phonons is effective (Fig. 1), the excitation of FE’s in the vicinity of the bottom of the exciton band with simultaneous creation of LO phonons should be allowed as well. This process is illustrated in Fig. 5(II). Depending on the energy of the excitation either the FE can be created in the vicinity of the bottom of the excitonic band [Fig. 5(II), curve *a*] or some more scattering events with acoustic phonons are necessary for the FE to reach thermal equilibrium [Fig. 5(II), curve *b*]. The relaxation via acoustic-phonon scattering may be either completed or not, depending on the ratio between scattering rate and FE lifetime. The question of whether the excitons reach thermal equilibrium with the lattice can be solved by study of the PLE spectra. If thermal equilibrium is not established, the excitons allowed to annihilate (with $k_{ex}=0$) can only be excited by light with energies equal to the energy of the bottom of exciton band plus nE_{LO} . Taking into account that the emission of phonons with \vec{q} of the order of $1/a_B$ is the most efficient process,²¹ in the PLE spectrum a set of narrow lines coinciding with the energy positions of the LO phonons with respect to the bottom of the exciton band should show up. Moreover, since excitons with any kinetic energy can recombine with emission of optical phonons, the PLE spectrum of the FE phonon replica should be quite different from that of the zero-phonon line. As can be seen from Fig. 4 this is clearly not the case. The width of the LO-phonon replicas is comparable to the energy of the LO phonon and cannot be explained by a dispersion of the LO-phonon branch. This implies efficient relaxation of hot excitons towards the bottom of the band via emission of acoustic phonons. The similarity of the PLE spectra for both zero- and one-phonon FE lines further indicates that thermal equilibrium in the FE gas is established. We found the identical Maxwellian shape for the 1LO and 2LO FE phonon replicas under excitation within and out of the region of PLE exciton resonances. This is additional support for our conclusion. Taking into account the very short FE lifetimes¹⁶ gives evidence for a very efficient interaction of FE’s with low energy acoustic phonons, providing the FE energy relaxation towards the bottom of the exciton band.

IV. SUMMARY

The investigation of phonon-assisted FE recombination in GaN has shown the important role of LO- and acoustic-phonon interactions in the dynamics of the FE annihilation process. From studies of the FE line shapes and from PLE spectra we have concluded that the energy relaxation process via scattering on the acoustic phonons is completed during the FE lifetime. Exciton formation in GaN occurs most efficiently in an indirect excitation process with the simultaneous emission of LO phonons.

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