Application of femtosecond-excitation correlation to the study of emission dynamics in hexagonal GaN

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(Received 14 April 1998)

We perform time- and spectrally resolved femtosecond-excitation correlation (FEC) on hexagonal GaN at 10 K. A general procedure to interpret the FEC signal at the exciton energies is presented. By fitting to a rate equation model, we find the bimolecular formation coefficient of the GaN A exciton to be $C=1.2\times10^{-18}$ cm^3 ps^{-1}. [S0163-1829(98)06439-X]

Since the first introduction of the population mixing or excitation correlation technique in 1981,[1,2] the technique has been applied successfully to the study of many systems. Depending on the width of the laser pulse, the technique is called either femtosecond-excitation correlation (FEC) or picosecond-excitation correlation (PEC). The wide availability of short pulse sources and the simplicity of the setup allows for widespread applications of both PEC and FEC in the study of tunnelling dynamics,[3,4] recombination lifetimes of excitons[5,6] and hot carriers,[7–9] and carrier sweepout time under an applied field.[10] In a typical experiment, two cross polarized excitation beams, chopped at two different frequencies, are used to excite the system. The time-integrated spectrally resolved photoluminescence is detected by a lock-in technique at the sum frequency as a function of time delay, δ, between the two pulses. Both the sign and magnitude of the signals provide information about the dynamics and nature of the emission process at the detection energy. In this paper, we report on a systematic study of epitaxy GaN film as a function of detection energies and excitation densities by temporally and spectrally resolved FEC. The purposes of our paper are to provide a simple interpretation to the FEC spectral lineshapes and temporal trace at different excitation densities at the exciton energy and to elucidate the dynamics of the different recombination mechanisms contributing to the GaN photoluminscence signal. For a review of recent advances in GaN, the readers are referred to the articles in Ref. 11.

The measurement is done using the second harmonic of a mode-locked Ti:sapphire laser with a pulse width of 180 fs and a repetition rate of 82 MHz. Assuming an absorption coefficient of 10^5 cm^{-1}, we estimate an excitation power of 1 mW is equal to a carrier density of 10^{17} cm^{-3}. The experiment is done at 10 K with the excitation wavelength tuned to an exciton binding energy, $E_b\simeq25$ meV, above the free A exciton transition, so that predominately cold $k=0$ free carriers are created. The photoluminscence is detected at the free and bound exciton energies using a SPEX 1401 double spectrometer with a cooled GaAs photomultiplier. The resolution of the spectrometer is set to 0.9 meV at 3.5 eV. The nominally undoped GaN film with a thickness of 3.3 μm is grown by metalorganic chemical vapor deposition (MOCVD). More information on the sample growth condition and material quality can be found in Refs. 12 and 13.

Both simple rate equations[3,8] and many-body calculations[14] have been applied to describe FEC results for the case of electron-hole recombination. On the other hand, little work has been done on the systematic experimental study on excitonic transitions using FEC in combination with theoretical calculation. Here we present a simple phenomenological model to interpret our results where the photoluminescence is predominately from free and bound excitons. The time-integrated FEC signal at energy E, $s(E,\delta)$, is given by the difference between the photoluminscence signal from the excitation by two pulses separated by time δ and twice the photoluminscence signal from excitation by one pulse[3,7,8] as given by

$$s(E,\delta)=PL(E,\delta)-2PL(E). \tag{1}$$

Note that $PL(E,\infty)=2PL(E)$. To a very good approximation, the photoluminscence signal, spectrally integrated for a transition, over a wide range of excitation power can be described phenomenologically as

$$PL(E)=aP^l, \tag{2}$$

where a is a proportionality constant, P is the total excitation power, and l is a number. Under the prescence of nonradiative recombination, it is expected that $l\neq1$. For example, in a bimolecular recombination process, $l=2$, whereas in an impurity related transition at high excitation, $l<1$, because of impurity saturation. Assuming the two pulses are of the same power, $\delta=0$, and combining Eqs. (1) and (2), the FEC signal is

$$s=a(2P)^l-2aP^l=2aP^l(2^{l-1}-1). \tag{3}$$

Thus, the FEC signal is proportional to the photoluminescence signal and is positive (negative) for superlinear growth, $l>1$ (for sublinear growth, $l<1$), and zero for linear growth, $l=0$. Note that the correlation signal is zero only for the spectrally integrated signal. The FEC spectrum of a single transition can be described by a normalized Gaussian distribution

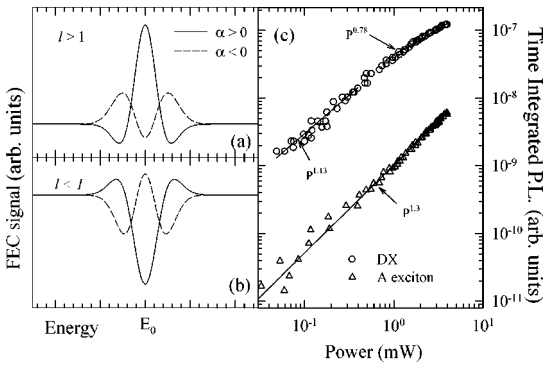

FIG. 1. (a) and (b) Theoretical FEC spectrum for a single transition and (c) integrated photoluminescence for the DX and the A excitons for different excitation power.

$$PL_G(E)=\frac{aP^l}{\Gamma}\sqrt{\frac{4\ln(2)}{\pi}}e^{-4\ln(2)[(E-E_0/\Gamma)]^2}, \qquad (4)$$

where $\Gamma=\Gamma_0+\alpha P$ and E_0 are the FWHM and center of the transition. We assume Γ increases linearly with excitation power due to power broadening. By definition, $\int dE\ PL_G(E)=aP^l$. Figure 1(a) shows a typical FEC spectrum assuming Eqs. (1) and (4) and a superlinear emission. For $\alpha>0$, which is the normal experimental condition, the transition exhibits a positive signal at the center E_0 and negative signals on the side due to the difference between the two Gaussian distributions of different linewidths. If E_0 is also a function of pump, then the FEC spectrum can be asymmetric and the areas of the negative signal are not the same. Figure 1(b) shows the FEC spectrum for a sublinear emission. For $\alpha>0$, the spectrum exhibits a negative signal at the center and positive signals on the side. The observation of a sign change in the FEC spectrum is applicable in general not only for a Gaussian peak given by Eq. (4) but also for any emission peak provided that there exists some form of broadening mechanism, i.e., $\alpha\neq 0$.[15]

Figure 1(c) shows the time-integrated photoluminscence intensity of the donor bound exciton (DX) and free A exciton as a function of excitation power. The DX line exhibits a superlinear increase of photoluminscence with power at low excitation density, $l=1.13$, and a sublinear increase of photoluminscence at high excitation density, $l=0.78$, due to saturation. On the other hand, the A line exhibits a superlinear increase of photoluminscence at all excitation densities. The value of $l=1.3$ suggests that both geminate formation from the initially created correlated electron-hole pairs and bimolecular formation from thermalized electron-hole pairs are important in the formation of the A exciton.[16] At low density, the DX population is proportional to the A exciton population and increases superlinearly. Figure 2 shows the time-integrated photoluminscence, $PL(E)$, and FEC spectra at different excitation densities. The dominant transitions are the acceptor bound (AX), DX, free A and B excitons. For comparison, the photoluminscence is normalized to unity. With increasing excitation density, we observe a broadening of the linewidths of the transitions and an increase of the free exciton emission relative to the DX emission, suggesting a heating of the excitons due to exciton-exciton and exciton-carrier scattering. The corresponding FEC traces for $\delta=0$

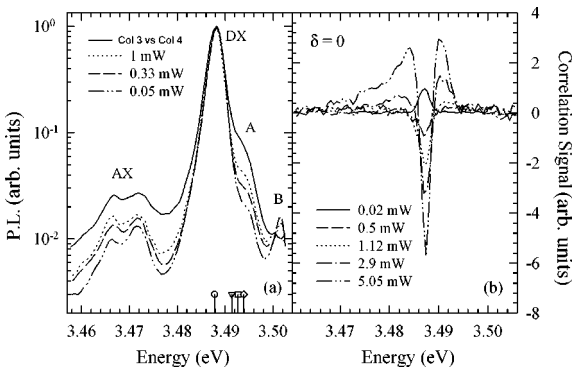

FIG. 2. (a) Normalized photoluminescence and (b) FEC spectrum for different excitation powers.

show a positive signal at low density due to the superlinear photoluminscence at the DX energy and a negative signal at high density due to the sublinear photoluminscence. The shape of the FEC spectra is very similar to that in Fig. 1(a) and 1(b) for $\alpha>0$, and we interpret the positive sidebands of the FEC signals to be caused predominately by the density-dependent broadening of the DX line and heating of the free exciton.

It is instructive to consider the characteristic time scales in the experiment and to compare each of these times with theoretical calculations or with other semiconductors such as GaAs. Typical carrier-carrier scattering times in GaN are expected to be comparable to those in GaAs and of the order of 200 fs at a density above 10^{15} cm^{-3}. Thus the carriers after pulse excitation can be approximated as an ideal Fermi gas characterized by a temperature. In addition, the 2D exciton formation time for a GaAs quantum well is 8 ps for a carrier density of 2×10^{10} cm^{-2},[3] so that we expect a similar value for GaN. The radiative e-h recombination time is given by[17]

$$\tau_0=\frac{6\pi\varepsilon_0 m_0 c^3\hbar^2}{e^2 n_r E_g}\left(\frac{m_0}{2p_{cv}^2}\right).$$

Assuming $n_r=2.67$, $E_g=3.508$ eV, and $2p_{cv}^2/m_0\simeq 7.7$ eV,[18] we have $\tau_0=0.96$ ns for GaN which can be compared to $\tau_0=0.58$ ns of GaAs. Since the dominant emission at low temperature is excitonic, we expect from the above argument that the conversion rate from free e-h pairs to excitons is fast in comparison to the lifetime of the e-h population at our excitation density regime.

We consider next the experimental time-resolved FEC signal. Figure 3(a) shows the time evolution for a fixed power excitation of 1 mW at different detection energies. The detection energies are also shown in Fig. 2(a). We observe a negative signal at the DX energy and a positive signal at the A exciton energy. All signals exhibit a dip at $\delta\sim 50$ ps and decay to zero within a time of about 100 ps. This is very different from time-resolved photoluminescence (TRPL) measurements, which show that the DX and A excitons decay monoexponentially with an approximate time of 136 and 66 ps, respectively. According to Eq. (1), a positive (negative) FEC signal means a stronger (weaker) time-integrated signal when the system is excited by two pulses delayed by a short time δ than when the system is excited by two pulses delayed by infinite time. The evolution of the

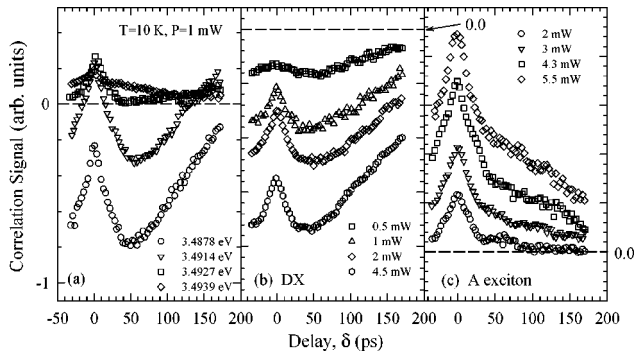

FIG. 3. (a) FEC signal for different detection energies and FEC signal for different excitation powers at (b) the DX exciton, and (c) the A exciton energies as a function of time delay.

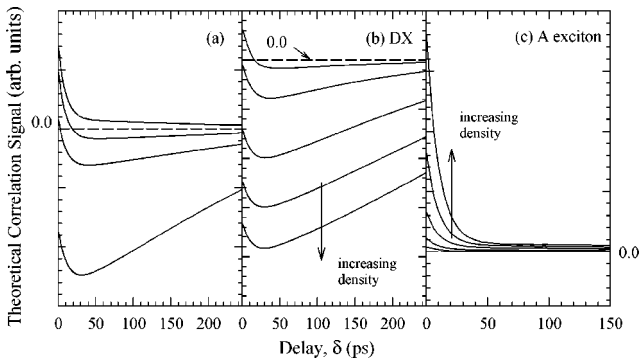

FIG. 4. (a) Theoretical FEC signal corresponding to the case of Fig. 3(a). Theoretical FEC signal for different excitation powers at (b) the DX exciton and (c) A exciton energies as a function of time delay for a density of $n_0=84, 56, 35, 21, 3\times10^{16}$ cm^{-3}.

FEC trace for different energies is complicated, primarily because there are various overlaps between the DX and A lines at these energies, and we concentrate here on the detection energies at the DX and A excitons. Figures 3(b) and 3(c) shows the time evolution for different excitation densities at the DX and A energies. The DX signal, $s_{DX}(\delta)$, is negative at $\delta=0$ which is caused by saturation of the DX population and by a subsequent conversion of the DX population to free excitons by scattering from carriers generated by the second pulse. $s_{DX}(\delta)$ decreases further up to $\delta=50$ ps which can be interpreted as the recovery time of the DX population and eventually returns to zero. For the A exciton signal, $s_A(\delta)$, we observe a positive peak at $\delta=0$ caused by buildup of the A population due to the saturation of the DX and the bimolecular formation of excitons from e-h pairs. $s_A(\delta)$ decays to zero in two time scales. The first time scale is the recovery time of the saturated DX population, and the second time scale is equal roughly to the A exciton lifetime. Physically, we expect $s_A(\delta)$ to follow the exciton population when excited by a single pulse.

To model our results, we use a set of rate equations for a two-level system coupled to an ideal Fermi gas. The population of the DX and A exciton is determined by the carrier population. The conversion of excitons to e-h pair requires phonon absorption and is unlikely at low temperature. Neglecting diffusion and surface effects, the electron density is governed by the Boltzmann equation of the form

$$\frac{dn}{dt}=P(t,\delta)-\frac{n(E)}{\tau_n(E)}+\int dE'\rho(E,E')n(E')p(E'), \tag{5}$$

where $P(t,\delta)$ is the pump term, τ_n is an effective carrier lifetime, and $\rho(E,E')$ is the matrix element which describes the process of radiative recombination and phonon-assisted carrier thermalization to form an exciton. A similar equation can be written for the hole density. Instead of solving Eq. (5), which requires detailed knowledge of the recombination process in $\tau_n(E)$ and material parameters in $\rho(E,E')$, we shall simplify the problem by assuming that the carrier population decays with a characteristic time τ_c so that

$$n(t,\delta)=p(t,\delta)=n_0(e^{-t/\tau_c}\theta(t)+e^{-(t-\delta)/\tau_c}\theta(t-\delta)), \tag{6}$$

where $n(t,\delta)$ $(p(t,\delta))$ is the electron (hole) density, n_0 is proportional to the pump, and $\theta(t)$ is the step function. Note that τ_c implicitly includes both radiative and nonradiative recombinations. To limit the number of fitting parameters, we assume the electron and hole have the same lifetime. The populations of the DX exciton, N_{DX}, and the A exciton, N_A, are described by

$$\frac{dN_{DX}}{dt}=-\frac{N_{DX}}{\tau_{DX}}+\frac{N_A}{\tau_t}\left(\frac{N_{DX0}-N_{DX}}{N_{DX0}}\right),$$

$$\frac{dN_A}{dt}=G(t,\delta)-\frac{N_A}{\tau_A}-\frac{N_A}{\tau_t}\left(\frac{N_{DX0}-N_{DX}}{N_{DX0}}\right), \tag{7}$$

where $\tau_{DX(A)}$ is the lifetime of the DX (A) exciton, τ_t is the trapping time of the free exciton, and N_{DX0} is the donor concentration. The driving term is given by $G(t,\delta)=Cn(t,\delta)p(t,\delta)$, where C is the bimolecular formation coefficient. It is expected that exciton formation occurs even at room temperature since $E_b\sim k_BT\sim25$ meV at room temperature. In addition, we neglect exciton-carrier scattering and geminate formation of excitons. The latter process which involves the same e-h pair generated by a single photon does not contribute to the FEC signal because it is filtered out by the lock-in. To obtain a reasonable value for the parameters of our rate equation, we first solve Eq. (7) for the case of single pulse excitation, $\delta=0$. The values of the decay times, $\tau_{DX,A,t,c}$, are adjusted so that the population decay fits the results obtained from TRPL measurements under low-energy excitation conditions. In addition, we fix $N_{DX0}=10^{17}$ cm^{-3}, which equals the measured background carrier density.[12] Finally, we calculate FEC traces for different excitation densities and adjust τ_A and C to match the theoretical results to the experimental results (Fig. 3). From Eq. (1), the DX (A) exciton FEC signal is given by $s_{DX(A)}(\delta)\propto\int dt[N_{DX(A)}(t,\delta)-N_{DX(A)}(t,\infty)]$. Figure 4 shows the theoretical FEC trace using the parameters: $\tau_{DX}=150$ ps, $\tau_A=100$ ps, $\tau_c=10$ ps, $\tau_t=50$ ps, and $C=1.2\times10^{-18}$ cm^3 ps^{-1}. Despite the simplicity of our model, the theoretical results qualitatively match that of the experimental results. A negative peak at the DX line at $\delta=0$ which is a characteristic of sublinear photoluminescence is observed in Fig. 4(b) due to population saturation. The same saturation effect along with the bimolecular formation process causes a peak at the A exciton signal at $\delta=0$, which is a characteristic

of superlinear photoluminscence. From simulations using different parameters, we find that the decay time of $s_{DX}(\delta)$ to zero increases with increasing values of τ_{DX} and τ_A. Physically, we expect $s_{DX}(\delta)$ to decay at a similar time scale as that of $N_{DX}(t)$ when excited by a single pulse. We note that the major discrepancy between theory and experiment is that the theoretical $s_A(\delta)$ decays only in a single time scale whereas we observe experimentally two time scales. We attribute the second time scale to carrier-exciton and exciton-exciton scatterings which provide a mechanism to convert DX to A excitons. Such ionization is not in our model and cannot be easily incorporated into our rate equation. In our model, we have also neglected reabsorption or polariton effects which can lead to an overestimate of the population density. Despite the shortcomings, we believe a fitting of the TRPL and FEC signal gives us a good estimate of the bimolecular formation coefficient in GaN. Finally, we note that our model can be extended to calculate the FEC signal for different detection energies. To a good approximation, the FEC signal at a given energy and fixed excitation density is given by $s(E)=a_{DX}s_{DX}(\delta)+a_A s_A(\delta)$, where $a_{DX,A}$ are weighting factors determined by the amount of DX and A exciton contribution to the photoluminescence. Figure 4(a) shows the theoretical FEC trace calculated using $a_{DX,A}$ extracted from photoluminescence data. Reasonable agreement is found between experiment and theory which shows the general trend of a negative to positive signal change when going from the DX to the A exciton energy.

In conclusion, we have performed a systematic study of GaN decay by FEC measurement. The nonlinearities which lead to the FEC signal are predominately caused by bimolecular formation of excitons and saturation of trap states. By using a simple phenomenological rate equation model, we fit our experimental results for different detection energies and excitation densities and obtain the various decay times of the system along with an estimate of the bimolecular formation coefficient of the A exciton in GaN.

We thank K. Rother and H. Klann for technical support, and S. Hallstein and K. Korona for critical comment on the manuscript.

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