Coherent exciton–biexciton dynamics in GaN

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(Received 24 September 2001; revised manuscript received 29 January 2002; published 22 April 2002)

Spectrally resolved and time-integrated four-wave mixing are used to measure the polarization dependence of biexcitonic signals and quantum beats between two-*A*-exciton ($X_AX_A^*$) and *A*-biexciton (X_AX_A) states in a high-quality GaN epilayer. Mixed beats with two periods are observed: the first beating period corresponds to the energy splitting between $X_AX_A^*$ and X_AX_A; the second period corresponds to beating between *A* excitons (X_A) and donor bound excitons (D^0X). We also measure the polarization-dependent *B*-biexciton (X_BX_B) signal. The effective masses for the *A* and *B* holes are deduced from the binding energy.

DOI: 10.1103/PhysRevB.65.193102 PACS number(s): 71.35.Gg, 78.55.Cr, 78.47.+p

Recent studies revealed that excitonic nonlinearities are modified by biexcitonic contributions, and exciton-biexciton interactions should be taken into account.[1,2] Biexcitons have been studied in various semiconductors such as bulk CuCl,[3] ZnSe quantum wells,[4] and GaAs quantum wells.[1,5,6] GaN is strongly excitonic, with an exciton binding energy of $E_X \sim 25$ meV, which makes it an ideal material for the study of biexcitons. The band-edge optical properties are dominated by the pronounced excitonic resonances arising from the three closely spaced valence bands present in the GaN wurzite structure. Little is currently known about the biexcitons in GaN.[7–9] Because the energy difference between neutral donor-bound excitons (D^0X) and *A* biexcitons (X_AX_A) is very small, the spectral broadening present in photoluminescence measurements makes it difficult to spectrally resolve the two features. However, the beating period determined by transient degenerate four-wave mixing (DFWM) yields an accurate splitting of the resonances, hence giving the binding energies for both D^0X and X_AX_A. The nonlinear interaction involved in the exciton dynamics cannot be described by a simple assembly of two-level systems; rather a five-level model has been suggested, including the two-exciton state as well as the biexciton state.[1,2] In particular, Saiki *et al.*[10] suggested that the use of cross-linear polarization is a good measure for detecting the two-photon coherence of the two-exciton state. This has been measured previously in GaAs[5] and ZnSe quantum wells.[4] In this paper, we report on quantum beat measurements between two-exciton and biexciton states in GaN with a cross-linear polarization. Additionally, by measuring the dephasing of the beats, the temperature dependence of the interaction with acoustic phonons has been determined. We have also measured the *B*-biexciton (X_BX_B) signal in GaN for the first time, to our knowledge.

Spectrally resolved (SR) DFWM and time-integrated (TI) DFWM measurements were made as a function of delay time and temperature using cross-linear and cocircular polarized light. A mode-locked Ti:sapphire laser with a 120-fs pulse width was frequency doubled in a beta-barium-borate crystal. The second-harmonic pulse width was estimated to be 167 fs by the Gaussian transform of its spectral width. The pump beam was focused to a 50-μm spot diameter onto a sample mounted in a closed-cycle helium cryostat kept at 15 K. We used a two-pulse self-diffraction configuration in reflection geometry. In this configuration, the coherent interaction of two excitation laser pulses, time delayed by τ with respect to each other and with wave vectors $\vec{k}_1$ and $\vec{k}_2$, generates a third-order nonlinear polarization. This polarization gives rise to an electric field coherently emitted into the phase-matched direction $2\vec{k}_1$-$\vec{k}_2$. The DFWM beams were modulated at two different frequencies, and the spectrally resolved diffracted signal was detected at the sum frequency using a photomultiplier connected to a lock-in amplifier; a monochromator was used in order to remove scattered luminescence. The GaN sample was a nominally undoped epilayer grown by lateral epitaxial overgrowth.[11]

Figure 1(a) shows the time-integrated photoluminescence spectrum and the SR-DFWM signal measured at zero time delay with cross-linear and cocircular polarized light. It has already been shown that the dominant luminescence peak can be attributed to unresolved neutral donor-bound exciton (D^0X) emission and *A*-biexciton (X_AX_A) emission in GaN.[7] Emission due to biexcitons has already been confirmed by a superlinear increase of the emission intensity with increasing excitation power,[7] and by investigating the decay dynamics of the signal.[8] However, polarization-dependent four-wave mixing (FWM) can confirm the presence of biexcitons. The polarization-selection rules in exciton-biexciton FWM are explained by a five-level model, which consists of a ground state, two one-exciton states, a biexciton state, and a two-exciton state.[1,2] For an incident beam perpendicular to the plane of the sample, only transitions with $\Delta J_z = \pm 1$ are dipole allowed between the conduction and valence bands, giving rise to two one-exciton states ($|X^{\pm}\rangle$) which have different angular momenta $J_z = \pm 1$ respectively. Using cocircular polarization (either $\sigma^+\sigma^+$ or $\sigma^-\sigma^-$), a one-exciton state

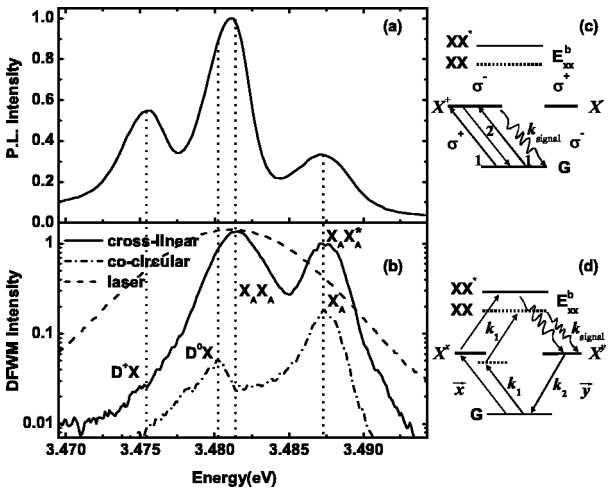

FIG. 1. (a) Photoluminescence spectrum measured at 15 K in GaN. (b) SR-DFWM spectrum measured at zero delay with cross-linear (solid) and cocircular (dot-dashed) polarized light. The broad dashed line shows the spectrum of the exciting laser, and that X_B and D^+X signals are negligible. Five-level model and optical transitions in FWM for cocircularly (c) and cross-linearly (d) polarized exciton bases.

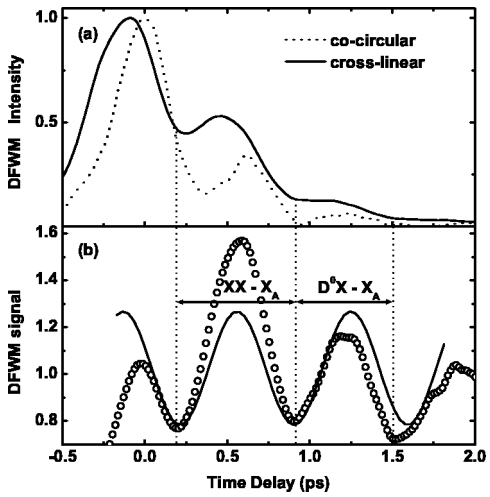

FIG. 2. (a) TI-DFWM signal as a function of delay time with cross-linear and cocircular polarized light. (b) The residual modulation signal (open circles) is taken by removing the exponential decay term from (a), a fitting function (solid) having a period of the X_AX_A-X_A beats is compared with the data (open circles).

($|X^+\rangle$ or $|X^-\rangle$) can be selectively excited, as shown in Fig. 1(c). The DFWM signal of biexcitons is forbidden for excitation with cocircular polarized light, and thus only the one-exciton state signal (X_A) is observable via the two-level process because of the polarization selection rules [Fig. 1(c)].[2] Indeed, the spectrum shown by the dotted line in Fig. 1(b) with cocircular polarized light does not show a biexcitonic signal, although a signal from D^0X is present. However, a strong biexcitonic signal (X_AX_A) appears when cross-linear polarization is used, represented by the solid line in Fig. 1(b). In the case of linear polarization, equivalent one-exciton states of $|X^x\rangle$ and $|X^y\rangle$, which correspond to $\vec{x}$ and $\vec{y}$ polarizations respectively, can be obtained by a linear basis transformation,[1] as shown in Fig. 1(d). For cross-linear polarizations, only the three-level process is allowed [Fig. 1(d)], while both the two- and three-level processes are possible for colinear polarization according to the five-level model.[2,10] Since our laser linewidth is wider than the biexciton binding energy, the two-exciton state ($X_AX_A^*$) and biexciton state (X_AX_A) are generated coherently via a two-photon absorption process with the $\vec{x}$-polarized $\vec{k}_1$ beam. The interference of the $\vec{k}_1$ beam with the $\vec{y}$-polarized $\vec{k}_2$ beam gives rise to a self-diffracted signal, where $X_AX_A^*$ and X_AX_A states are de-excited by emitting $\vec{y}$-polarized beams, as shown in Fig. 1(d). The two resonance signals observed with cross-linear polarization in Fig. 1(b) correspond to the $X_AX_A^*$-X_A and X_AX_A-X_A transitions, respectively.[12] The biexciton binding energy is measured to be 5.83 ± 0.10 meV. This value is comparable to recently reported X_AX_A binding energies of 5.7 meV (Refs. 8 and 9) for wurtzite GaN, and quite similar to a calculated binding energy of 5.8 meV, based on Huang's model.[13] The DWFM signal from ionized donor bound excitons is also very weak, despite its strength in the photoluminescence spectrum.

Figure 2(a) shows the TI-DFWM signal as a function of time delay at the X_AX_A energy with cross-linear and cocircular polarized light. Both DFWM signal intensities are normalized for comparison, and the original signal intensity ratio is $I_{\rm cross}/I_{\rm co}=6.25$. With cocircular polarized light, the decay of this signal for $T_L=15$ K shows an oscillation with a period of 579 ± 2 fs. This beat period corresponds to an energy splitting between D^0X and X_A of $\Delta E=h/\tau=7.14\pm0.10$ meV, the D^0X binding energy. However, with cross-linear polarized light, the DWFM signal is modulated by the interference of two separate beat periods of X_AX_A-$X_AX_A^*$ and D^0X-X_A. The B-exciton signal is eliminated by a careful tuning of the laser. To measure the beating periods more precisely, the decay signal was removed by dividing the data by an exponential decay term [Fig. 2(b)], and a function $f(\tau)=A\sin^2[\pi(\tau+\delta)/T_{XX-XX*}]+B$ (solid line), having the period of the X_AX_A-$X_AX_A^*$ beating was compared with the measured data. As is apparent from the figure, the two different beat periods are clearly mixed. The first beat period of 709 ± 2 fs corresponds exactly to the X_AX_A binding energy (5.83 ± 0.10 meV), while a second beat period of 579 ± 2 fs corresponds to the D^0X binding energy (7.14 ± 0.10 meV). Bearing in mind the fact that the X_AX_A signal is much larger than that of the D^0X in the SR-DFWM spectrum, the oscillation intensity of the X_AX_A should be dominant during the early part of the beating signal, and the D^0X beating signal would be masked. However, the X_AX_A linewidth is wider than that of the D^0X, implying that the X_AX_A signal decays faster than the D^0X. As a result, the D^0X beating signal becomes more evident as the time delay between pump and probe increases.

It is known that no beatings due to biexcitons are present in the TI-DFWM signal in a homogeneous system. If a beat is observed at positive delay times in a homogeneous system, the signal is attributed to fifth-order contributions.[2] We established that the DFWM signal was proportional to the third

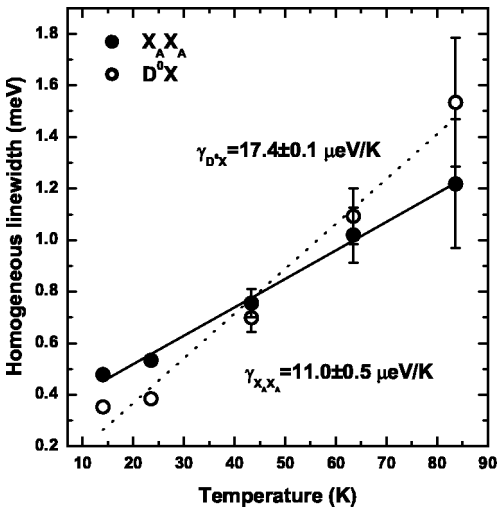

FIG. 3. Lattice temperature dependence of the homogeneous linewidth of X_AX_A and D^0X in GaN, deduced from TI-DFWM decay rates, assuming that both processes are inhomogeneously broadened.

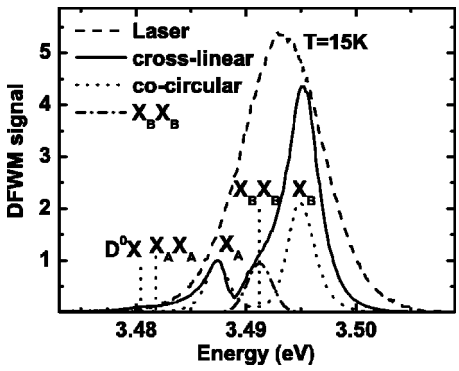

FIG. 4. SR-DFWM spectrum measured at zero delay with cross-linear (solid) and cocircular (dotted) polarized light when the laser is tuned between the X_A energy and that of X_B. Note that the *B*-biexciton signal disappears with co-circular polarized light. The X_BX_B signal (dot-dashed) is extracted by using a Gaussian fit to the line shape.

power of the intensity of the incident beams, which indicates that contributions from higher-order nonlinear processes are negligible, and that our experimental results can be described in terms of the third-order optical susceptibility. On the other hand, in an inhomogeneous system, a deep beat due to macroscopic polarization interference is not possible; rather a quantum beat due to quantum-mechanical interference created by coherent mixing of two states with a small energy difference is observable.[14,15] Consequently, these facts lead us to conclude that the beat with cross-linear polarization in Fig. 1(b) is a case of quantum beats between $X_AX_A^*$ and X_AX_A in an inhomogeneous system as shown schematically in Fig. 1(d).

A stronger DFWM signal is observed at negative time delays with cross-linear polarized light than with cocircular polarized light. This may be due either to exciton-exciton interactions[16] or to a two-photon coherence (TPC)-induced biexcitonic signal.[17] It has been reported that exciton-exciton interactions become dominant in GaN above 5×10^{15} cm^{-3} (Ref. 18); we estimate the density of *A* excitons in our experiment to be 2×10^{15} cm^{-3}, which was deduced using an absorption coefficient at the *A*-exciton energy of 8.90×10^4 cm^{-1}.[18] Thus we suggest that the DFWM signal at negative delay times is mainly due to a TPC-induced biexcitonic signal. The phase shift between cross-linear and cocircular polarizations has been measured in other materials,[2,15] and described theoretically.[2]

Both beating signals appear at positive delay times and have large linewidths in the SR-DFWM spectrum. This implies that these transitions are inhomogeneously broadened. In this case, the decay time of the DFWM signal T_d is equal to one-quarter of the exciton dephasing time, $T_d=T_2/4$,[18] and the homogeneous linewidth ($\Gamma^{\rm hom}=2\hbar/T_2$) can be deduced as shown in Fig. 3. Usually the temperature dependence of the homogeneous linewidth due to phonon scattering can be described by $\Gamma^{\rm hom}=\Gamma^{\rm hom}(0)+\alpha T+\beta[\exp(\hbar\omega_{LO}/k_BT)-1]^{-1}$, where α and β are the acoustic- and optical-phonon coefficients, respectively, and $\Gamma^{\rm hom}(0)$ represents temperature-independent impurity scattering. However, due to a large LO-phonon energy (92 meV) in GaN, the last term is negligible in our low-temperature regime (<90 K). The smaller $\Gamma^{\rm hom}(0)$ value of D^0X at low temperatures implies slower dephasing, and it can be understood qualitatively in the following way. A lighter biexciton moves through the lattice and has a higher probability of scattering with defects. However, a bound exciton is localized on the defect and oscillates in phase with the generating light field. As a result, the phase of the bound exciton is destroyed more slowly than that of the biexciton. This fact is also consistent with our result in Fig. 2(b), that the X_AX_A signal decays faster than the D^0X. In addition, it has been reported that biexciton-phonon scattering is twice as fast as exciton-phonon scattering due to a larger deformation potential.[6] The measured acoustic-phonon coefficient at X_AX_A ($\gamma_{XX}=11.0\pm0.5$ μeV/K) is more than twice of that at X_A ($\gamma_X=3.5$ μeV/K) reported in GaN.[19] We also found that D^0X has a larger acoustic-phonon coefficient ($\gamma_{D^0X}=17.4\pm0.1$ μeV/K) than X_AX_A ($\gamma_{XX}=11.0\pm0.5$ μeV/K). This implies that D^0X may have a larger deformation potential than X_AX_A, because the D^0X is more localized in the lattice.

In a further measurement, we tuned the laser to an excitation energy between that of X_A and X_B. The DFWM signal obtained is shown in Fig. 4. With cross-linear polarized light, the solid line exhibits a shoulder between the X_A and X_B signals. However, this signal disappears with cocircular polarized light. This polarization dependence supports the assertion that the shoulder with cross-linear polarization arises from the *B* biexciton (X_BX_B), and that this DFWM signal does not arise from X_AX_B, since this would not disappear when excited by cocircular polarized light.[20] A binding energy for the X_BX_B of (3.80 ± 0.01 meV) is obtained, and we deduce an effective mass for the *B* hole of 1.03 m_0, which is slightly lighter than that for the *A* hole (1.30 m_0).

In conclusion, we have performed femtosecond SR-DFWM and TI-DFWM spectroscopy on a high quality GaN

epilayer. With cocircular polarized light, we measured only the D^0X-X_A quantum beats. However, with cross-linear polarized light, we found that two beats (D^0X-X_A and $X_AX_A^*$-X_AX_A) are mixed with different dephasing rates, and that each beat period corresponds exactly to the binding energy. We found that the strength of acoustic-phonon interactions with the D^0X is stronger than that with the X_AX_A by analyzing the temperature-dependent homogeneous linewidth. Finally, we have confirmed the existence of the *B* biexciton, and binding energies of X_AX_A and X_BX_B are measured. We also obtained effective masses of the *A* and *B* holes, and found that the *B*-hole effective mass is slightly lighter than the *A*-hole effective mass.

We are grateful to J. Park for his computational support.

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