Influence of Exciton-Exciton Interaction on Quantum Beats

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Spectrally resolved four-wave mixing measurements in wurtzite GaN show a dependence of the quantum beats' phase on incident polarizations. We observe different phases at the *A*-exciton and the *B*-exciton resonances when exciting with circular polarized light. The observed phase difference indicates that exciton-exciton interaction plays a major role in the quantum beat process. The developed analysis allows us to conclude that the spins of the electrons rather than the holes give the major contribution to the exciton-exciton interaction in GaN. [S0031-9007(99)08944-9]

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Quantum beats of excitons have been observed in four-wave mixing (FWM) experiments in various semiconductors [1–3]. In these experiments, two exciton transitions are simultaneously excited and the time-integrated FWM (TI-FWM) signal, measured as a function of delay time between the excitation pulses, oscillates with a period corresponding to the energy difference of the two excitons. In contrast to atomic systems, the origin of the quantum beats in semiconductors is complicated because of the many-body Coulomb interaction among the photoexcited carriers which gives rise to the optical nonlinearity in semiconductors. At high excitation densities the manifestation of this many-body interaction in the optical response has been successfully explained by the semiconductor Bloch equations [4] which are based on a mean field approximation. In the low-density regime, however, experimental observations reveal the importance of four-particle correlations for the third-order optical nonlinearity [5] which requires a treatment on the basis of the microscopic density matrix equations and the dynamics-controlled truncation scheme [3,6].

However, as long as we are concerned only with a region close to a stable excitonic resonance in the low-density regime, we can account for four-particle correlations as two-body exciton-exciton interaction by rewriting the electron-hole Hamiltonian in terms of bosonic exciton operators [7,8]. This simplifies the treatment of the four-particle correlations at the semiconductor band edge drastically and is effective for a system where excitons are stable and have a large binding energy. Recently the FWM process in semiconductor microcavities has been explained using the weakly interacting boson (WIB) model [9–12]. Within the WIB model the anharmonicity of the electron-hole system is due to a spin-dependent interaction of optically active excitons [8]. This interaction gives rise to the polarization dependence of the third-order optical response at the semiconductor band edge and, in turn, to the dependence of the FWM signal on the polarization of the incident beams. In the case of quantum beats both amplitude and phase are polarization sensitive, and, correspondingly, may be employed to study the spin-dependent exciton-exciton interaction. Up to now, the phase of the quantum beats has been studied only in co-linear (excitation beams are equally linearly polarized) and cross-linear (excitation beams are orthogonally linearly polarized) polarization configurations [1–3]. In both of these configurations, cosinelike quantum beats have been observed and the phase of the beats shows a π shift when going from co-linear to cross-linear.

We extend these earlier studies by using circular polarized excitation and report the observation of a polarization-dependent phase of the quantum beats from excitons in wurtzite GaN, where excitons have a large binding energy of about 26 meV [2]. We observe different phases in the co-linear, cross-linear, and co-circular (excitation beams are of the same circular polarization) configurations. In contrast to the co- and cross-linear configurations, the quantum beats in the co-circular configuration show pronounced sine components and different phases at the *A*- and *B*-exciton resonances. These experimental findings can be explained by spin-dependent interactions between the *A* and *B* excitons and indicate that the polarization-dependent phase shift is a sensitive probe for the exciton-exciton interaction.

Wurtzite-GaN layers with a thickness of 100 μm are grown by vapor-phase epitaxy on a sapphire substrate [13]. After growth the substrate is removed. As reported in our previous work [2], excitons are homogeneously broadened in this sample. The sample is mounted in a closed-cycle helium cryostat and kept at 14 K in all measurements. We use a Kerr lens mode-locked Ti:sapphire laser producing 120 fs pulse at a repetition rate of 76 MHz. The second harmonic pulse is generated in a beta-barium-borate crystal and it excites both the *A* exciton and *B* exciton simultaneously. In TI-FWM measurements we use the two-pulse self-diffraction geometry

[14] in reflection. The signal is spectrally resolved with a monochromator. The zero position of the delay T between the two incident pulses is determined by monitoring both signal directions $2\mathbf{k}_1 - \mathbf{k}_2$ and $2\mathbf{k}_2 - \mathbf{k}_1$.

In order to confirm that the measurements are performed in the $\chi^{(3)}$ regime, we examine the dependence of the signal on the excitation intensity and find that the FWM signal is proportional to the third power of the intensity of the incident beams. This indicates that contributions from fifth- and higher-order nonlinear processes to the TI-FWM signal are negligible and that our experimental results can be described in terms of the third-order optical susceptibility.

The TI-FWM signal in the direction $2\mathbf{k}_1 - \mathbf{k}_2$ at the A- and B-exciton resonance is shown in Fig. 1(a) for the co-linear, cross-linear, and co-circular polarization configuration. Clear beats are observed in all polarization configurations at each resonance. The beat period of 0.65 ps corresponds to the energy separation between the A exciton and B exciton of about 6 meV.

The TI-FWM signal from homogeneously broadened excitons at the frequency of the A or B exciton as a function of the time delay T can be expressed as $I_{A,B}^{ij} \propto [1 + a_{A,B}^{ij}\cos(\Omega T - \phi_{A,B}^{ij})]\exp(-2\gamma T)$, where the subscripts A and B indicate the exciton, and superscripts $(ij = xx, xy, \sigma\sigma)$ label the co-linear, cross-linear, and co-circular polarization configurations, respectively; γ is the exciton dephasing rate. The beating contrast $a_{A,B}^{ij}$ is as high as 90% for the xx and xy configurations and nearly 60% for the $\sigma\sigma$ configuration: $a_{A,B}^{xx} \approx a_{A,B}^{xy} \approx 0.9$, $a_{A,B}^{\sigma\sigma} \approx 0.6$. For the xx and xy configurations, the signal has a π-phase difference (compare with [1–3]) but is nearly the same for the A and B excitons, $\phi_A^{xx} \approx \phi_B^{xx} \approx 0.1\pi$ and $\phi_A^{xy} \approx \phi_B^{xy} \approx -0.9\pi$. However, in the $\sigma\sigma$ configuration the phase is different, $\phi_A^{\sigma\sigma} = 0.5\pi$ and $\phi_B^{\sigma\sigma} = -0.2\pi$. The data presented in Fig. 1(a) allow us to obtain the phase of the beats with an accuracy of $\pm 0.1\pi$ [15]. Importantly, the phase of the quantum beats in $\sigma\sigma$ configuration is neither 0 nor π for both excitons. This pronounced sine component of the beats indicates a contribution of the exciton-exciton interaction to the TI-FWM signal.

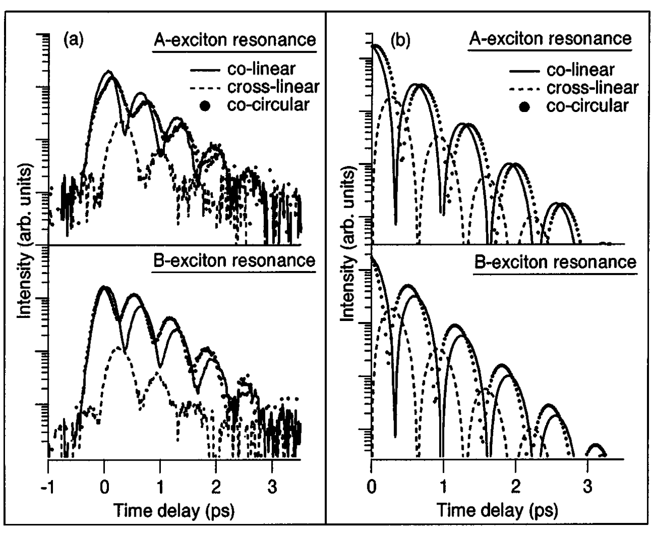

FIG. 1. (a) Measured FWM signals in the direction $2\mathbf{k}_1 - \mathbf{k}_2$ as a function of time delay T at the resonance of the A exciton and the B exciton for co-linear (solid line), cross-linear (dotted line), and co-circular (circle) incident polarizations taken at 14 K. Positive time delay is defined as pulse k_2 arriving first. (b) TI-FWM signal calculated under the assumption of 100% beat contrast in the xx and xy configurations. The ratio of the parameters is $\gamma\nu{:}R{:}W{:}\gamma_{\mathrm{EID}} = 1{:}1{:}-9{:}9$.

In order to describe the polarization dependence of the phase, we extend the standard bosonic representation of the electron-hole Hamiltonian [7] to a system with two types of excitons and employ the WIB model [9,11,12]. Within the WIB model framework, the composite nature of the excitons gives rise to the exciton-exciton interaction and results in an anharmonicity of the exciton themselves and their coupling with photons.

By extending the treatment developed in [11] to a system with two types of excitons, the electron-hole Hamiltonian, which accounts for the interaction between optically active excitons, can be written as $H_x = H_{AA} + H_{BB} + H_{AB}$. H_{AA} and H_{BB} describe the contribution to the Hamiltonian from the A and B excitons, respectively,

$$H_{AA} = \sum_{\sigma}\left(\omega b_{A\sigma}^{\dagger} b_{A\sigma} + \frac{v_0}{V}\frac{R}{2} b_{A\sigma}^{\dagger} b_{A\sigma}^{\dagger} b_{A\sigma} b_{A\sigma}\right) + \frac{v_0}{V} W b_{A+}^{\dagger} b_{A-}^{\dagger} b_{A+} b_{A-} \tag{1}$$

(H_{BB} has the same form as H_{AA} with the replacement $A\pm \to B\pm$), while H_{AB} is due to the interaction between them:

$$H_{AB} = \frac{v_0}{V} R_{AB} b_{A\sigma}^{\dagger} b_{A\sigma}^{\dagger} b_{B\sigma} b_{B\sigma} + \frac{v_0}{V} W_{AB}(b_{A+}^{\dagger} b_{B-}^{\dagger} b_{A+} b_{B-} + b_{B+}^{\dagger} b_{A-}^{\dagger} b_{B+} b_{A-}). \tag{2}$$

In (1) and (2), $b_{A,B\pm}$ are exciton annihilation operators for the A and B excitons with angular momentum $\sigma\pm$, V is the crystal volume, and $v_0 = \pi a_B^3$, where a_B is the Bohr radius. We have adopted the single mode approximation in (1) and (2) by assuming that the excitons keep their wave vectors imparted by the incident beams throughout the FWM process under resonant excitation. The wave vector indices have been dropped in (1) and (2) for simplicity.

The first term in (1) represents the harmonic part of the excitonic Hamiltonian of the A exciton. The anharmonic part of H_x is of fourth order in $b_{A,B\pm}$ and accounts for spin-dependent exciton-exciton interactions. The second term in (1) accounts for the interaction between excitons of the same type [hereafter these will be abbreviated as A-A (B-B) interactions]. H_{AB} describes the interaction between A and B excitons with same (R_{AB}) and opposite (W_{AB}) spins (A-B interactions). Note that the A and B

excitons in GaN have nearly the same Bohr radius and transitional dipole moment. For the sake of simplicity we have assumed in (1) and (2) that A-A and B-B interactions can be described by the same anharmonic parameters, i.e., $W_{AA} = W_{BB} = W$ and $R_{AA} = R_{BB} = R$.

The composite nature of the excitons also results in the anharmonicity of the exciton-photon coupling Hamiltonian H_{int} and manifests itself as the phase-space filling (PSF) [16] effect. Within the WIB framework this effect can be accounted for by decreasing the transitional dipole moment between states where two electrons (and holes) have the same spin. For a system with two types of excitons the exciton-photon coupling Hamiltonian is $H^{\mathrm{int}} = H_A^{\mathrm{int}} + H_B^{\mathrm{int}} + \mathrm{H.c.}$, where $H_{A,B}^{\mathrm{int}}$ describes the interaction of the A and B excitons with the light wave. The exciton-photon coupling Hamiltonian for the A exciton is given as

$$H_A^{\mathrm{int}} = -\mu E_+ e^{-i\omega t} b_{A+}^\dagger \left(1 - \frac{v_0}{V}\nu b_{A+}^\dagger b_{A+} - \frac{v_0}{V}\nu' b_{B-}^\dagger b_{B-}\right) - \mu E_- e^{-i\omega t} b_{A-}^\dagger \left(1 - \frac{v_0}{V}\nu b_{A-}^\dagger b_{A-} - \frac{v_0}{V}\nu' b_{B+}^\dagger b_{B+}\right). \tag{3}$$

Here $\mu = \sqrt{V/v_0}\,\mu_{cv}$ is the exciton dipole moment, μ_{cv} is the interband dipole moment, and E_σ is the electric field amplitude with σ polarization. In (3), ν and ν' account for the reduction of the dipole coupling due to the finite population of the one-exciton states. H_B^{int} can be obtained from (3) by replacing $A\pm$ with $B\pm$. In order to account for the fact that in the states $b_{A\pm}^\dagger b_{A\pm}^\dagger|0\rangle$ and $b_{B\pm}^\dagger b_{B\pm}^\dagger|0\rangle$ both electrons and holes have the same spin, while in the states $b_{A\pm}^\dagger b_{B\mp}^\dagger|0\rangle$ only electrons have the same spin, we have introduced in (3) different PSF factors ν and ν' for each case. The effects of excitation induced dephasing (EID) [17] can also be accounted for in the WIB model by increasing the dephasing rates for transitions between one-exciton states and two-exciton states from γ to $\gamma + (v_0/V)\gamma_{\mathrm{EID}}$ while those between ground states and one-exciton states remain γ [10–12].

The complex amplitude of the excitonic polarization can be obtained from (1)–(3) by using the standard density matrix approach. Keeping all terms linear in anharmonic parameters we arrive at a closed set which describes the temporal evolution of the excitonic polarizations $P_{A,B\pm}$, populations of the one-exciton states $N_{A,B\pm} = \langle b_{A,B\pm}^\dagger b_{A,B\pm}\rangle/V$, and expectation values of the other second- and third-order products of $b_{A,B\pm}$. Here $\langle\cdots\rangle$ stands for statistical averaging. In particular, the equation for $P_{A\pm}(\omega)$ reads

$$\begin{aligned}\left[\frac{\partial}{\partial t} + i(\omega_A - \omega) + \gamma\right]P_{A\pm}(\omega) - \frac{i\mu_{cv}^2}{\hbar v_0}E_\pm = &-\frac{2i\nu\mu_{cv}^2}{\hbar}(2N_{A\pm} + N_{B\mp})E_\pm - \frac{2i\nu'\mu_{cv}^2}{\hbar V}\langle b_{B\pm}^\dagger b_{A\pm}\rangle E_\mp \\ &- i(R - i\gamma_{\mathrm{EID}})\mu_{cv}\sqrt{\frac{2v_0}{V^3}}\langle b_{A\pm}^\dagger b_{A\pm}^\dagger b_{A\pm}\rangle \\ &- i(R_{AB} - i\gamma_{\mathrm{EID}})\mu_{cv}\sqrt{\frac{v_0}{V^3}}\langle b_{A\pm}^\dagger b_{B\pm}^\dagger b_{B\pm}\rangle \\ &- i(W - i\gamma_{\mathrm{EID}})\mu_{cv}\sqrt{\frac{v_0}{V^3}}\langle b_{A\pm}^\dagger b_{A\mp}^\dagger b_{A\mp}\rangle \\ &- i(W_{AB} - i\gamma_{\mathrm{EID}})\mu_{cv}\sqrt{\frac{v_0}{V^3}}\langle b_{A\pm}^\dagger b_{B\mp}^\dagger b_{B\mp}\rangle.\end{aligned} \tag{4}$$

All terms on the right-hand side of this equation are of third order in the electric field. In order to calculate the third-order optical response the expectation values $\langle b_{A\pm}^\dagger b_{B\pm}^\dagger b_{B\pm}\rangle$, etc., on the right-hand side of (4) should be replaced by those for a system of two harmonic oscillators. Equation (4) shows the contributions from the different mechanisms of the excitonic nonlinearity. The first three terms on the right-hand side are due to the PSF effect. The other terms are due to spin-dependent exciton-exciton interaction.

The solution of the equations for the expectation values gives us the amplitudes of the A- and B-excitonic polarizations. For example, in the $\sigma\sigma$ configuration the WIB model gives the following expression for the TI-FWM signal with δ-pulse excitation at the A-exciton resonance:

$$I_A^{\sigma\sigma} \propto \left(1 + \frac{2(1+\alpha)\cos\phi_{AA}\cos\phi_{AB}}{\cos^2\phi_{AB} + (1+\alpha)^2\cos^2\phi_{AA} + \alpha^2\cos^2\phi_{AA}\cos^2\phi_{AB}}\cos(\Omega T - \phi_A^{\sigma\sigma})\right)e^{-2\gamma T}, \tag{5}$$

where $\alpha = 2\nu\gamma/\gamma_{\mathrm{EID}}$, $\tan\phi_{AA} = R/(\gamma_{\mathrm{EID}} + 2\nu\gamma)$, $\tan\phi_{AB} = R_{AB}/\gamma_{\mathrm{EID}}$, and $\phi_A^{\sigma\sigma} = \phi_{AA} - \phi_{AB}$. Note that without exciton-exciton interaction we get $\phi_A^{\sigma\sigma} = 0$ and, therefore, no sine component of the beats. Since $\phi_A^{\sigma\sigma} = (0.4 \pm 0.1)\pi > 0$ [15], we conclude that exciton-exciton interaction and EID give contributions of the same order of magnitude to the FWM signal and $R > [1 + 2\nu(\gamma/\gamma_{\mathrm{EID}})]R_{AB}$.

We also find the dependence of the contrast and phase of the quantum beats in the xx and xy configurations on R, W, R_{AB}, W_{AB}, ν, and ν'. In these configurations the experiment shows nearly 100% contrast of the quantum beats, $a_{A,B}^{xx} \approx 1$ [see Fig. 1(a)], while $\phi_{A,B}^{xx} = 0$ and $\phi_{A,B}^{xy} = \pi$ [15]. By substituting these values into the WIB equations, we arrive at $\nu = \nu'$, $R = W_{AB}$, and $W = R_{AB}$. With the conditions $R > 0$ and $W < 0$, which have been

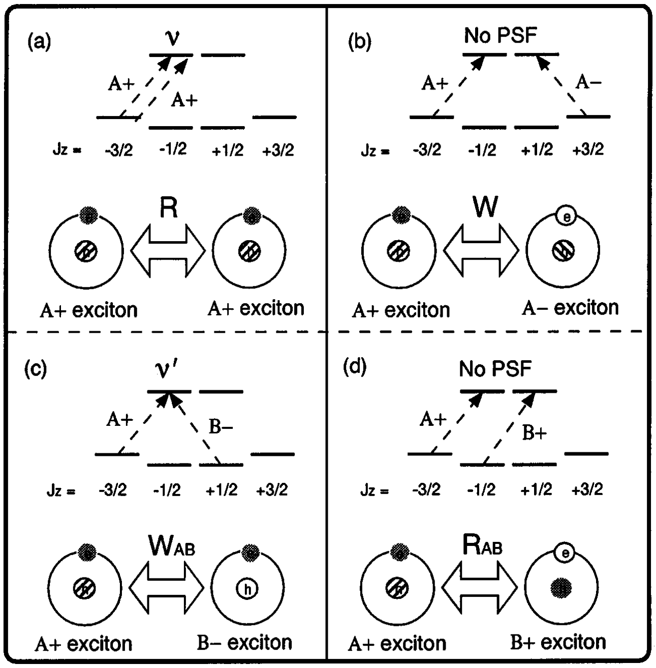

FIG. 2. Schematic of the correspondence of the PSF factors ν and ν' and the interaction energies R, W, R_{AB}, and W_{AB} to the combination of two excitons. The upper part of each figure describes the spins of the electrons and holes of two excitons. (a) Two $A+$ excitons: the spins of both holes and electrons are the same. The PSF factor is ν and the interaction energy is R. (b) $A+$ and $A-$ excitons: the spins of both holes and electrons are different. There is no PSF effect and the interaction energy is W. (c) $A+$ and $B-$ excitons: only the spin of the electrons is the same. The PSF factor is ν' and the interaction energy is W_{AB}. (d) $A+$ and $B+$ excitons: the spins of both holes and electrons are different. There is no PSF effect and the interaction energy is R_{AB}.

obtained theoretically [8] and experimentally [9–11], we could conclude that, in GaN, A and B excitons with the same angular momentum attract each other while those with opposite angular momentum repel each other; $R_{AB} < 0$ and $W_{AB} > 0$. Such a conclusion is consistent with the inequality $R > [1 + 2\nu(\gamma/\gamma_{\mathrm{EID}})]R_{AB}$ which has been obtained independently from the results of the $\sigma\sigma$ configuration. The above relationships between anharmonic parameters suggest that the electron spins play a major role in exciton-exciton interaction. Indeed, the difference between ν and ν' arises from the fact that in the states $b^\dagger_{A\pm}b^\dagger_{A\pm}|0\rangle$ and $b^\dagger_{B\pm}b^\dagger_{B\pm}|0\rangle$ both electrons and holes have the same spin, while in the states $b^\dagger_{A\pm}b^\dagger_{B\mp}|0\rangle$ only electrons have the same spin (see Fig. 2). Therefore, $\nu = \nu'$ implies that electron spins are more important in exciton-exciton interaction than the hole spins.

In summary, we have studied the polarization dependence of the quantum beats in GaN from homogeneously broadened excitons in the third-order regime. An intermediate phase is observed in a co-circular polarization configuration. We treat the four-particle correlations as a spin-dependent exciton-exciton interaction in the analysis and show that this interaction determines the phase of the quantum beats.

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[15] It is necessary to note that the phases of the beats at the A- and B-exciton resonances should have opposite sign ($\phi_A^{ij} = -\phi_B^{ij}$) only for excitation with ideal δ pulses. Our numerical simulation shows that a finite pulse width results in a departure from such a symmetry. For our experimental conditions the calculation yields that the finite pulse width results in a phase offset of about 0.1π. By subtracting this offset from the measured values given in the text we arrive at the phase which has to be compared with the theory: $\phi_A^{xx} \approx \phi_B^{xx} \approx (0 \pm 0.1)\pi$, $\phi_A^{xy} \approx \phi_B^{xy} \approx (1.0 \pm 0.1)\pi$, $\phi_A^{\sigma\sigma} \approx (0.4 \pm 0.1)\pi$, and $\phi_B^{\sigma\sigma} \approx -(0.3 \pm 0.1)\pi$.
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