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Influence of exciton-exciton interactions on frequency-mixing signals in a stable exciton-biexciton system

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Transient nondegenerate four-wave mixing was performed in the femtosecond domain on a stable exciton-biexciton system. For excitation with two spectrally narrow pulses of frequencies ω_1 and ω_2 that have no spectral overlap with each other, only a frequency-mixing signal at $2\omega_1 - \omega_2$ was observed. The polarization dependence of the frequency-mixing signal intensity changed dramatically with increasing frequency difference between the incident pulses. Our results demonstrate that the frequency-mixing signal is strongly correlated with the exciton dynamics and the dramatic change of its polarization dependence is caused by the exciton-exciton interactions.

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Recently, extensive studies have demonstrated that exciton-exciton interactions play important roles in the nonlinear optical responses on semiconductor quantum wells.[1–4] Polarization-dependent degenerate four-wave mixing (DFWM) measurement in the femtosecond domain[5–11] is generally used to investigate exciton-exciton interactions such as the biexciton formation (BIF),[6–9] the excitation-induced dephasing (EID) (Refs. 7–11) effects, etc.

Nondegenerate FWM (NFWM) spectroscopy[12,13] has received considerable attention because of its great advantages: (i) the independent tunability of incident pulses provides additional information for the physical processes in the nonlinear response, (ii) the NFWM signal can be measured with the high signal-to-noise ratio, since the NFWM spectral position is away from the spectral positions of incident pulses. Quite recently, there have been a few reports of NFWM experiments in the coherent femtosecond domain.[13–16] Ahn *et al.*[15] have performed a NFWM experiment using two independently tunable femtosecond pulses in the exciton resonance region on a GaAs multiple quantum well (MQW). They first focused on a frequency-mixing signal at $2\omega_1 - \omega_2$, which is distinguished from the exciton resonant signal. In their case, the BIF effect was ignored owing to the small biexciton binding energy of the GaAs MQW, and the frequency-mixing signal was not directly correlated with the exciton dynamics, in contrast with the exciton resonant signal. To our knowledge, NFWM experiments have never been performed in a stable exciton-biexciton system where biexciton binding energy is much larger than the broad bandwidth of a femtosecond pulse. Therefore, the influence of exciton-exciton interactions such as the BIF effect on the frequency-mixing signals is not yet known. Furthermore, although there are many studies of the polarization dependence of the DFWM signal around the exciton resonance, the polarization dependence of the frequency-mixing signal of NFWM in the femtosecond domain has never been measured.

In this paper, we report the results of a polarization-dependent NFWM experiment using two-color femtosecond pulses on a self-organized quantum-well material $(C_6H_{13}NH_3)_2PbI_4$, which is a stable exciton-biexciton system with a large biexciton binding energy ($\simeq$44 meV).[17] We show that, even in the exciton resonant region, only a frequency-mixing signal appears for excitation with two spectrally narrow (8-meV bandwidth) pulses that have no spectral overlap with each other. We measure the polarization dependence of the frequency-mixing signal intensities by varying the frequency difference between two pulses. We demonstrate that the polarization dependence shows a dramatic change with increasing frequency difference between the incident pulses, and we find that the frequency-mixing signal is strongly correlated with the exciton dynamics. It is noted that the frequency-mixing signal is influenced by the exciton-exciton interactions not only in the exciton resonant region but also in the off-resonant frequency region. We also show that a simple calculation based on a seven-level phenomenological model[18] can reproduce our experimental results.

$(C_6H_{13}NH_3)_2PbI_4$ forms an ideal two-dimensional system, where inorganic well layers are composed of a two-dimensional network of corner-sharing $[PbI_6]^{4-}$ octahedra between organic barrier layers of alkylammonium chains.[19,20] Due to the quantum and dielectric confinement effects,[21] excitons are tightly confined in the inorganic well layers. Consequently, they have an extremely large binding energy ($\simeq$400 meV) and oscillator strength ($\simeq$0.7 per formula unit).[20,22,23] Moreover, biexcitons also have a large binding energy ($\simeq$44 meV),[17] which is larger than the spectral width of our femtosecond pulses. Our previous DFWM investigations have shown that the exciton energy in the spin-coated film has slightly inhomogeneous broadening.[24]

The samples used in this experiment were 50-nm-thick polycrystalline films spin-coated on optically flat glass substrates. The films were highly oriented with the inorganic well layers parallel to the substrate surface. Each sample was kept at a temperature of 12 K for all measurements. A two-pulse self-diffraction geometry was used, where incident pulses with wave vectors $\boldsymbol{k}_1$ and $\boldsymbol{k}_2$ were separated by a time

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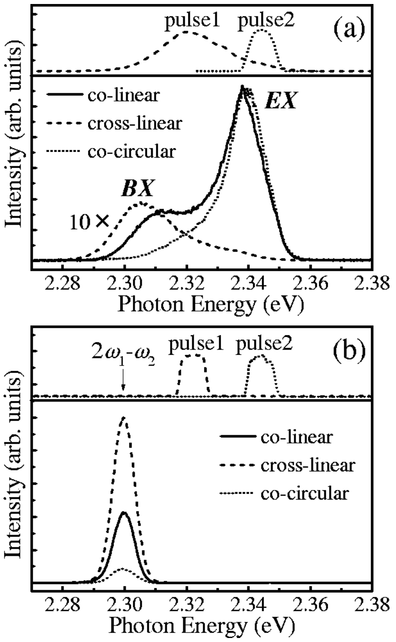

FIG. 1. Spectra of the NFWM signal at $\tau=0$ in the colinear (solid line), cross-linear (dashed line), and cocircular (dotted line) configurations when ω_1 is tuned to 22 meV below $\Omega_{\rm ex}$ and ω_2 is tuned to $\Omega_{\rm ex}$. The bandwidth of $\boldsymbol{k}_2$ pulse is 8 meV, and $\boldsymbol{k}_1$ pulse has (a) 22 meV and (b) 8 meV bandwidths.

delay τ. The NFWM signal in the direction $2\boldsymbol{k}_1-\boldsymbol{k}_2$ was spectrally resolved by a combination of a spectrometer and a CCD camera. The light sources were two synchronized optical parametric amplifiers seeded by the pulses from a common amplified mode-locked Ti:Al$_2$O$_3$ laser (Coherent RegA9000). The center frequencies of two incident pulses could be tuned to ω_1 and ω_2 independent of each other. In all measurements, ω_2 was kept at the exciton resonance 2.344 eV ($\Omega_{\rm ex}$), and the bandwidth of the $\boldsymbol{k}_2$ pulse was narrowed to 8 meV (see Fig. 1) by a spectral filter with a grating pair and a slit. The intensity of the incident pulses was sufficiently weak so that the signal intensity had a cubic dependence on the incident power, which confirmed that our experiment was performed under the $\chi^{(3)}$ limit. The intensity of the $\boldsymbol{k}_2$ pulse was approximately 1.3 MW/cm^2, which corresponds to the exciton density of 10^9 cm^{-2} for all measurements.

Figure 1(a) shows the spectra of NFWM signals at $\tau=0$ with various polarized incident pulses. The $\boldsymbol{k}_1$ pulse has approximately a 22-meV bandwidth and is centered 22 meV below $\Omega_{\rm ex}$, as shown at the top of Fig. 1(a). The spectrum of the $\boldsymbol{k}_1$ pulse and that of the $\boldsymbol{k}_2$ pulse are partially overlapped. We observe a strong peak in the spectrum around $\Omega_{\rm ex}$ [labeled EX in Fig. 1(a)] and another peak [labeled BX in Fig. 1(a)] at 40 meV below $\Omega_{\rm ex}$ in a colinear (incident pulses have the same linear polarization) configuration. The energy difference between the BX and EX peaks corresponds to the biexciton binding energy estimated by a photoluminescence measurement at high excitation density.[17] The BX peak intensity shows a relative increase in a cross-linear configuration (incident pulses have orthogonal linear polarization) and a strong suppression in a cocircular (incident pulses have the same circular polarization) configuration. The spectral position and the polarization dependence of the BX peak confirm that the BX signal is attributed to the biexciton-exciton transition. The EX signal is dominant in the colinear and cocircular configurations, since the $\boldsymbol{k}_1$ pulse has a spectral overlap with the $\boldsymbol{k}_2$ pulse at $\Omega_{\rm ex}$, which leads to the DFWM process via the exciton.

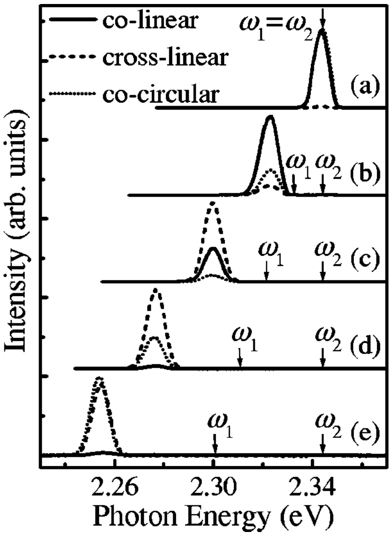

FIG. 2. Spectra of the NFWM signal at $\tau=0$ at various ω_1 when $\omega_2=\Omega_{\rm ex}$ in the colinear (solid line), cross-linear (dashed line), and cocircular (dotted line) configurations. (a) $\omega_1=2.344$ eV, (b) $\omega_1=2.333$ eV, (c) $\omega_1=2.322$ eV, (d) $\omega_1=2.311$ eV, (e) $\omega_1=2.300$ eV. Spectra are normalized to the maximum intensity at each ω_1.

For complete NFWM measurements, we applied a spectral filter to narrow the bandwidth of the $\boldsymbol{k}_1$ pulse to 8 meV [see Fig. 1(b)] so that the spectral overlap between the $\boldsymbol{k}_1$ pulse and the $\boldsymbol{k}_2$ pulse could be ignored. Figure 1(b) shows the spectra of the NFWM signals at $\tau=0$ in the various configurations, where the center frequencies ω_1 and ω_2 are the same as in Fig. 1(a). Compared to Fig. 1(a), the EX signal disappears, and only a frequency-mixing signal at $2\omega_1-\omega_2$ is observed. This result indicates that spectral overlap is important for the exciton resonant signal, agreeing with the previous study.[13,15]

We measured the polarization dependence of the spectra of the NFWM signals at various values of ω_1, while keeping ω_2 at $\Omega_{\rm ex}$. Figure 2 shows the spectra at $\tau=0$ normalized to the maximum intensity at each value of ω_1. In our measurements, only the frequency-mixing signal is observed at exactly $2\omega_1-\omega_2$ in any polarization configuration and at any value of ω_1. The polarization dependence of the frequency-mixing signal intensity changes drastically with ω_1. At $\omega_1=2.344$ eV ($=\Omega_{\rm ex}$), i.e., the degenerate case [Fig. 2(a)], the frequency mixing is equivalent to the exciton resonant signal, where the signal intensity in the colinear configuration $I_\parallel$ is almost equal to that in the cocircular configuration $I_{\sigma\sigma}$, and the intensity in the cross-linear configuration $I_\perp$ is considerably smaller. This result suggests that the signal is mainly induced by the EID effect.[10,11] At $\omega_1=2.322$ eV

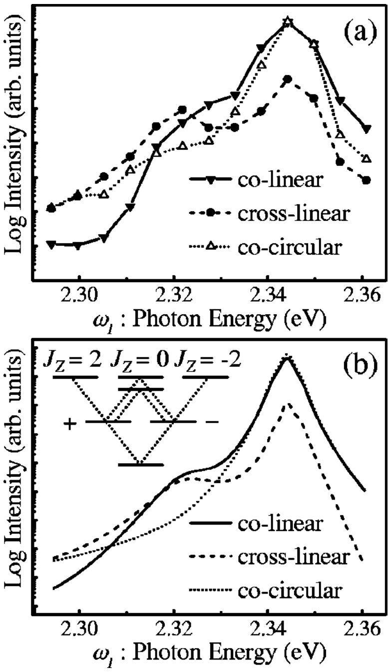

FIG. 3. (a) The frequency-mixing signal intensity at $\tau = 0$ as a function of ω_1 when $\omega_2 = \Omega_{\mathrm{ex}}$ in the colinear (solid reverse triangle), cross-linear (solid circle), and cocircular (open triangle) configurations. (b) Calculated curves for $\nu = 0.12$, $\gamma_E/\gamma = 3.0$, $|\mu_b|^2/|\mu|^2 = 0.33$. Inset: a schematic of a seven-level system.

[Fig. 2(c)] with the same condition as in Fig. 1(b), $I_\perp$ is almost twice as large as $I_\parallel$, in striking contrast to the result of $\omega_1 = 2.344$ eV [Fig. 2(a)]. A strong suppression of $I_{\sigma\sigma}$ indicates that this dramatic change in the polarization dependence of the frequency-mixing signal is attributed to the BIF effect. At $\omega_1 = 2.300$ eV [Fig. 2(e)], $I_\parallel$ is much smaller than $I_\perp$ and $I_{\sigma\sigma}$, which are nearly equal. It should be noted that the frequency-mixing signal intensity greatly depends on the polarization configuration even in the frequency region away from both the exciton and biexciton resonances.

We were also interested in the dependence of the frequency-mixing signal intensity on the value of ω_1. Figure 3(a) plots the frequency-mixing signal intensity at $\tau = 0$ normalized to the cube of the incident power as a function of ω_1 in the various polarization configurations. In all configurations, the intensities reach maximum values at the exciton resonance Ω_{ex} and drop suddenly with increasing detuning from Ω_{ex}. $I_\perp$ has another clear peak at the biexciton two-photon resonance (Ω_{TPR}). This means that coherent emission through the biexciton-to-exciton transition can occur even if there is no spectral overlap between incident pulses. Note that this process is fundamentally different from the process contributing to the BX signal in Fig. 1(a). In the narrowband measurement [Fig. 1(b)], the biexciton state is excited through the two-photon transition with degenerate $\boldsymbol{k}_1$ pulses, while in the broadband measurement [Fig. 1(a)], the biexciton state is created mainly through a combination of the ground-to-exciton and exciton-to-biexciton transitions. This fact indicates that the polarization dependence of the BX peak in Fig. 1(a) is different from that in Fig. 1(b).

To clarify the role of exciton-exciton interactions in the polarization dependence, we analyze the results of Fig. 3(a) based on a few-level density-matrix description of the third-order excitonic nonlinearity.[18] We consider a seven-level system [as shown in the inset of Fig. 3(b)] including the ground, one-exciton ($J_z = \pm 1$), biexciton ($J_z = 0$), and free two-exciton ($J_z = \pm 2{,}0$) states,[25] where the phase-space filling (PSF), EID, and BIF effects are introduced phenomenologically. The PSF effect is taken into account by decreasing the dipole moment of the transition from a one-exciton state with $J_z = \pm 1$ to a free two-exciton state with $J_z = \pm 2$ by a fraction ν as $\sqrt{2}(1-\nu)\mu$. The EID effect is taken into account by introducing an additional dephasing γ_E to the exciton dephasing γ for the transition from a one-exciton to a free two-exciton state, i.e., $\gamma + \gamma_E$. We assume that the sum of the squares of the transition dipole moments from a one-exciton state to two-exciton states with $J_z = 0$ is conserved,[26] i.e. $|\mu'|^2 + |\mu_b|^2 = |\mu|^2$, where μ' and μ_b are the transition dipole moments from the one-exciton state to the free two-exciton state with $J_z = 0$ and to the biexciton state, respectively. According to this model, if there is no interaction between excitons, i.e., $\nu = \gamma_E = \mu_b = 0$, the signal disappears because of the bosonic property of excitons.

We calculate the intensities of the NFWM signals for various ν, γ_E, and μ_b, using the third-order nonlinear optical susceptibility on the seven-level model. In the calculation, the exciton dephasing γ and the biexciton-to-ground dephasing γ_b are assumed to be 2 and 7 meV, respectively, as estimated from our previous DFWM experiment.[24] Moreover, we take into account exciton inhomogeneous broadening by assuming a Gaussian distribution of the exciton energy with a width of 9 meV, which was estimated from the present exciton absorption spectrum (not shown). A detailed description of the calculation is beyond the frame of this paper and will be published elsewhere. Figure 3(b) shows our calculated curves for $\nu = 0.12$, $\gamma_E/\gamma = 3.0$, $|\mu_b|^2/|\mu|^2 = 0.33$. It is found that Fig. 3(a) is well reproduced by the calculation.

To demonstrate the evidence of the influence of the PSF, EID, and BIF on the polarization dependence, we perform calculations under various conditions. Taking account only of the PSF effect, the signal ratio takes a constant value $I_\parallel : I_\perp : I_{\sigma\sigma} = 1:1:4$ at any ω_1. For only the EID effect, it leads to small $I_\perp$ compared to $I_\parallel \simeq I_{\sigma\sigma}$. In both cases, the signal ratio is almost independent of the value of ω_1 and no peak at Ω_{TPR} exists. For only the BIF effect, the peak at Ω_{TPR} appears, but $I_{\sigma\sigma}$ vanishes, and $I_\perp$ is equal to $I_\parallel$ at any ω_1. Thus, our analysis demonstrates that our experimental results cannot be reproduced if any of the PSF, EID, and BIF effects are not taken into account. Especially, it is proved that the dramatic change of the polarization dependence of the frequency-mixing signal intensity with respect to the value of ω_1 is induced mainly by the BIF effect.

In conclusion, we have performed a nondegenerate four-wave mixing experiment in a stable exciton-biexciton system and demonstrated that only the frequency-mixing signal is observed, whenever incident pulses have no spectral overlap. We have found that the relative intensities of the frequency-mixing signal with respect to the polarization configuration change drastically with the value of ω_1. Our calculated results based on a seven-level system, where the PSF, EID, and BIF effects are introduced phenomenologically, well reproduce the experimental results. Our results strongly indicate that these interactions significantly influence the polarization dependence of the frequency-mixing signal, showing that the measurement of the polarization dependence of the frequency-mixing signal can serve as an effective probe for exciton-exciton interactions.

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