Large Four-Wave Mixing of Spatially Extended Excitonic States in Thin GaAs Layers

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We study the size dependence of the nonlinear response of weakly confined excitons for the size region beyond the long wavelength approximation regime. The observed degenerate-four-wave mixing signal of GaAs thin layers exhibits an anomalous size dependence, where the signal is resonantly enhanced at a particular thickness region. The theoretical analysis elucidates that this enhancement is due to the size-resonant enhancement of the internal field with a spatial structure relevant to the nondipole-type excitonic state. These results establish the formerly proposed new type of size dependence of nonlinear response due to the nonlocality induced double resonance.

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There has been a great interest in the size-dependent optical nonlinearity of confined electronic systems for over a decade because the elucidation of its fundamental mechanism is expected to open the way for designing materials with the exceedingly effective nonlinear functions. Conventionally, the size-dependent nonlinear signal is discussed through the size dependence of the nonlinear susceptibility. It has been well discussed that the size dependence of the oscillator strength is reflected in that of the third order susceptibility $\chi^{(3)}$. In the strong confinement regime, the shrinkage of the electron-hole relative motion in 2D (quantum wells) or 1D (quantum dots) systems causes an enhancement of the oscillator strength [1,2], leading to the large nonlinear susceptibility. In the weak confinement regime, on the other hand, the coherent extension of the center-of-mass (c.m.) wave function causes the size-linear enhancement of the oscillator strength, which leads to the same behavior of the nonlinear susceptibility [3,4]. As we see in such examples, the picture that is based on the oscillator strength is useful to some extent. However, one should be reminded that this picture is valid for the limited size region, i.e., the region where the long wavelength approximation (LWA) holds. Especially, in the weak confinement regime, there can be conditions where the LWA is broken down. In such a case, the nonlocal response plays a central role, and the consideration of the degrees of freedom of the spatial variation of the radiation field is essential for the discussion of the size-dependent nonlinear response.

Recently, we have theoretically predicted an anomalous size dependence of the nonlinear response for the c.m. confinement regime by means of the nonlocal theory [5,6] considering the material with the large LT splitting (the splitting between the longitudinal and the transverse exciton energies) like CuCl, where the large nonlinear response of the spatially extended "nondipole-type" excitonic state is caused by the size-resonant enhancement of the internal field with a nanoscale spatial structure. In this effect, the resonant behavior of the self-consistent internal field reflecting that of the induced polarization strongly affects the size dependence of the nonlinear signal. On the other hand, the enhancement of the degenerate four-wave mixing (DFWM) signal has recently been observed experimentally for the GaAs thin layers with a particular thickness [7], which has a similar aspect to the above-mentioned effect. However, no evidence has been presented so far for linking the observed effect to the theoretical prediction. Especially, it has not been clear even theoretically whether the same effect as predicted for the I-VII material (CuCl) with the large LT splitting [5,6] can be seen for the different type of material like GaAs with the small LT splitting. If we could definitely link the observed effect to the proposed mechanism, it would provide not only the clear evidence of this mechanism for the first time, but also an understanding of the generality of the physics of this phenomenon. In this Letter, therefore, we experimentally trace the size dependence of the DFWM signal with a systematic sample preparation of GaAs thin layers, and analyze the results by means of the nonlocal theory with an appropriate model for GaAs to clearly confirm the new type of size dependence of the nonlinear response.

In the preparation of samples, we should pay special attention to realize the ultrahigh quality so that the coherence of the excitonic c.m. motion is well maintained in a whole sample. GaAs is a suitable sample material considering this point, for which the fabricating technique is well established. We prepare the double heterostructures of samples consisting of three layers of GaAs with equal thickness L which are divided by 5-nm-thick $Al_{0.3}Ga_{0.7}As$ layers. The layers are grown on a GaAs (100) substrate by molecular beam epitaxy. The reflectance spectrum near the Brewster angle for each sample is taken for the sake of the sample characterization. Figure 1(a) shows the observed spectra in the case of $L = 110$ nm in the vicinity of $1s$ exciton resonance. The very sharp peak structures are attributed to the quantized c.m. levels of excitons.

For the analysis of the linear response, we explicitly treat the c.m. motion of excitons confined in the film, where the film surface is assumed to be perpendicular to the Z axis. As for the relative motion of excitons, we

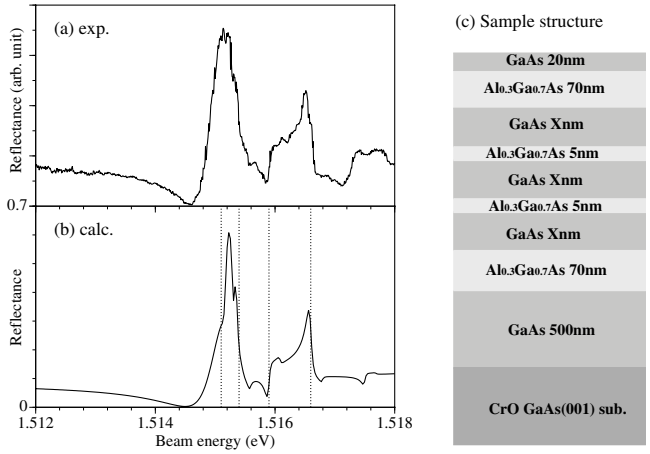

FIG. 1. (a),(b) The reflectance spectrum for $L = 110$ nm and (c) sample structure. The vertical dotted lines in (b) indicate the quantized excitonic levels determined in the theory. Used parameters are $\hbar\omega_T = 1.515$ eV, $\Delta_{\rm LT} = 0.17$ meV, $M = 0.5$, Γ of the top layer is 0.03 meV, $d_l = 117.6$ Å, and $\varepsilon_b = 12.56$.

treat it as that in the bulk whose effect is reflected in the parameter of the bare exciton-radiation coupling (e.g., LT-splitting $\Delta_{\rm LT}$). Since the experimental result of the linear response shows little contribution of the light hole excitons to the main peak structures near the lowest exciton level, we consider the contributions from the heavy hole excitons alone. The eigenfunctions and the eigenenergies of quantized c.m. levels can be written as $\Phi_{ex,\mathbf{K}_\parallel,n}(\mathbf{R}) = \sqrt{1/S}\exp(i\mathbf{K}_\parallel\mathbf{R}_\parallel)\sqrt{2/(L-2d_l)}\sin K_n Z$ and $E_{ex,\mathbf{K}_\parallel,n} = \hbar\omega_T + \hbar^2(K_\parallel^2 + K_n^2)/2M$, respectively, where S is the area of the film surface, d_l is the width of the homogeneous dead layer (HDL) [8], Z ($\mathbf{R}_\parallel$) and K_n ($\mathbf{K}_\parallel$) are the coordinate and wave vector perpendicular (parallel) to the film surface, respectively, $\hbar\omega_T$ is the exciton energy at the bottom of band, and M is the total mass. The allowed values of K_n are $n\pi/(L-2d_l)$ $(n = 1, 2, 3, \ldots)$. The matrix elements between the ground and one-exciton states are $\langle\Phi_{ex,n}|\hat{P}(Z)|0\rangle = I\sqrt{2/(L-2d_l)}\sin K_n Z$, where I has a relationship to $\Delta_{\rm LT}$ as $|I|^2 = \varepsilon_b\Delta_{\rm LT}/4\pi$, where ε_b is the background dielectric constant. We analyze the linear response with this model, applying the additional boundary condition (ABC) theory [9] to the case of the p polarization incidence.

Figure 1(b) shows the calculated spectrum for $L = 110$ nm. As shown in Ref. [10], the simplified c.m. confinement model plus HDL well reproduces the observed spectrum. From the fitting of the damping constant Γ, we find that (i) the spectral structure is dominated by the top layer because Γ of the second and third layers are pretty large, and that (ii) Γ of the top layer is around 0.03 meV, which indicates the excellent quality of the top layer.

The nonlinear signal has been measured for several samples with different values of L. By the above type of analyses, it has been verified that the change of Γ with sample is very little. We measure the DFWM signal using a two-pulse self-diffraction configuration, where the pulse width is 2 ps and its peak excitation intensity is set below 5 kW/cm^2 where the detected DFWM signal intensity shows a cubic dependence on the excitation intensity. The sample was kept at 5 K during measurements. Figure 2(a) shows the energy dependence of DFWM for several values of L. Remarkable thickness dependence is found; namely, the DFWM signal is strongly enhanced for $L = 110$ nm. The observed DFWM signal intensity for $L = 110$ nm is about 25 times larger than that of the bulk (1-μm-thick) sample [7]. In Fig. 2(b), we show the comparison between the DFWM intensities by the cross-linear and the colinear polarization measurements for $L = 110$ nm. The signal in colinear polarization measurement contains the contributions from both the one-exciton and the biexciton resonances, whereas that in the cross-linear measurement contains the contribution from biexciton resonance alone. The result shows little contribution from the biexciton resonance in the energy region where the signal is enhanced.

In the analysis of the nonlinear response, we consider the contributions from the state filling due to the Pauli exclusion effect and the exciton-exciton interaction. The former and latter effects appear at one-exciton and biexciton resonances, respectively. The role of the exciton-exciton correlation in the nonlinear response is now an active topic, and several model schemes are proposed [11–13]. In this analysis, we treat the contributions of two-exciton states in a simple way as explained below because the size dependence of the DFWM in the weak confinement regime is mainly determined by the one-exciton contributions. We consider the quantized c.m. motion of biexciton similar to the one-exciton states and limit ourselves to $\mathbf{K}_\parallel = 0$ subspace for both one- and two-exciton states assuming the normal incidence. The value of the matrix element arising from the wave functions of relative motion can be determined by the comparison between the signal intensities

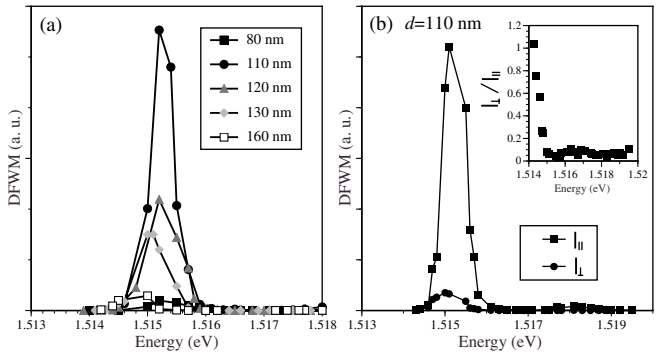

FIG. 2. (a) Energy dependence of the DFWM intensity for several values of L. The peak excitation intensity is set at 2.5 kW/cm^2. (b) Energy dependence of DFWM intensity by the cross- and colinear measurement for $L = 110$ nm. The inset indicates their ratio. The peak excitation intensity is set at 5 kW/cm^2.

with the cross-linear and the colinear polarization measurements. As for the scattering two-exciton states, we do not explicitly treat them because it is thought that the cancellation between the transitions of [ground state → one-exciton states] and the [one-exciton states → scattering two-exciton states] does not bring about strong thickness dependence of nonlinear signal arising in the considered thickness region [14,15], though this effect should be considered to obtain the absolute signal intensity.

The calculation of the DFWM signal is performed along the nonlocal theory of the nonlinear response [16], where we solve the Maxwell equation including the linear and nonlinear polarization written in the nonlocal form. The nonlocal linear polarization should be written in $P^{(1)}(Z;\omega) = \int \chi^{(1)}(Z,Z';\omega)\mathcal{E}(Z')\,dZ'$, where $\chi^{(1)}$ and $\mathcal{E}(Z)$ are the linear susceptibility and the field amplitude, respectively. $P^{(1)}$ and the third order nonlinear polarization $P^{(3)}$, which is written in a similar nonlocal form, can be rewritten in terms of the quantities defined as $F_n = \int_0^{L-2d_l} \sqrt{2/(L-2d_l)}\sin(K_n Z)\mathcal{E}(Z)\,dZ$ and similar one $F_{n\nu}$ for [one-excitons → two-excitons] transition by using the separable form of the susceptibility in respect with the coordinates [16]. The terms containing the resonance poles of transitions between the ground and one-exciton states in $P^{(3)}(Z;\omega_s = 2\omega_2 - \omega_1)$, for example, are written as

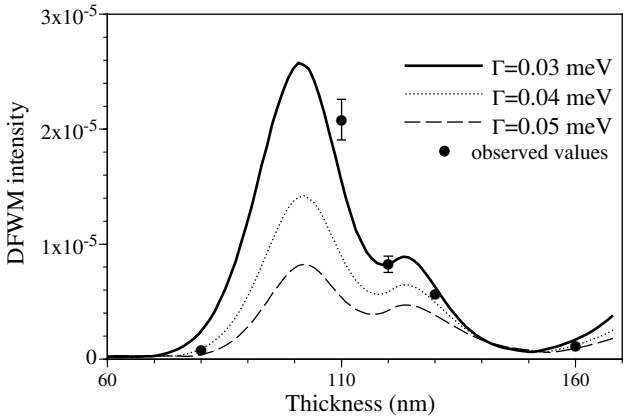

FIG. 3. The thickness dependence of the peak value of DFWM intensity. Closed circles are measured values in arbitrary unit. Solid line shows calculated values normalized by the incident probe intensity. The extent of the enhancement is affected by the nonradiative damping constant.

$$P^{(3)}(Z;\omega_s)_{0\to 1} = I^4\sqrt{\frac{2}{L-2d_l}}\sum_n \sin K_n Z \sum_m A(E_{ex,n},E_{ex,m};\omega_1,\omega_2)F_n^{(2)}F_m^{(2)}F_m^{(1)*}\exp(-i\omega_s t)\,, \tag{1}$$

where we pick up the contributions of the most (triply) resonant terms. In this expression, ω_1 and ω_2 are the test and pump frequencies, respectively. In the following calculation, we take $\omega_1 = \omega_2$. The amplitude of the internal field in $F_n^{(1)}(F_n^{(2)})$ is, as a good approximation, that of the test (pump) field obtained within the linear response calculation. The resonance poles are included in the factor $A(E_{ex,n},E_{ex,m};\omega_1,\omega_2)$. Besides these terms, there are the terms including the poles for the [one-exciton states–two-exciton states] transition and those for the two-photon absorption by the two-exciton states. The Maxwell equations are reduced to the simultaneous cubic equations to determine the constants $\{F_n\}$, $\{F_{n\nu}\}$, which are easily solved by using the Maxwell's boundary conditions for all the interfaces. Figure 3 shows the thickness dependence of the calculated DFWM signal together with the experimental results, where the peak value in the spectrum is indicated for each thickness. The theory very well reproduces the thickness dependence and the signal enhancement around $L = 110$ nm.

Examining the individual terms, we find that the signals are mainly from the one-exciton resonance whose poles are included in A in Eq. (1). The explicit expression of A is

$$\begin{aligned} A(E_{ex,n},E_{ex,m};\omega_1,\omega_2) = {} & \frac{1}{(E_{ex,n}-(2\omega_2-\omega_1)-i\Gamma)(\omega_2-\omega_1+i\gamma)}\left[\frac{1}{E_{ex,m}-\omega_1+i\Gamma}-\frac{1}{E_{ex,m}-\omega_2-i\Gamma}\right] \\ & + \frac{1}{(E_{ex,n}-(2\omega_2-\omega_1)-i\Gamma)(E_{nm}-(\omega_2-\omega_1)-i\Gamma_{nm})} \\ & \times\left[\frac{1}{E_{ex,n}-\omega_2-i\Gamma}-\frac{1}{E_{ex,m}-\omega_1+i\Gamma}\right], \end{aligned} \tag{2}$$

where $E_{nm} = E_{ex,n} - E_{ex,m}$. Note that $\{F_n\}$ in (1) is nothing but the amplitude of each component of the internal field when we expand $\mathcal{E}(Z)$ with the bases of the function $\sqrt{2/(L-2d_l)}\sin(K_n Z)$. Namely, F_2, for example, means the component associated with the second one-exciton state ($n = 2$). From the expressions (1) and (2), we understand that the transition to the nth one-exciton level is strengthened if F_n has a large value near the resonance pole of the nth level. Particularly, it should be emphasized that the large nonlinear signal around $L = 110$ nm arises from $n = 2$ exciton whose spatial structure is the quadrupole type (having one node in the surface normal direction), which is caused by the enhancement of F_2. Figure 4 shows the energy dependence of $|F_n|^2$ for $L = 110$ nm calculated within the linear response. It is found that $|F_2|^2$ is enhanced and has a sharp peak near the $n = 2$ exciton level, which is prominent particularly for

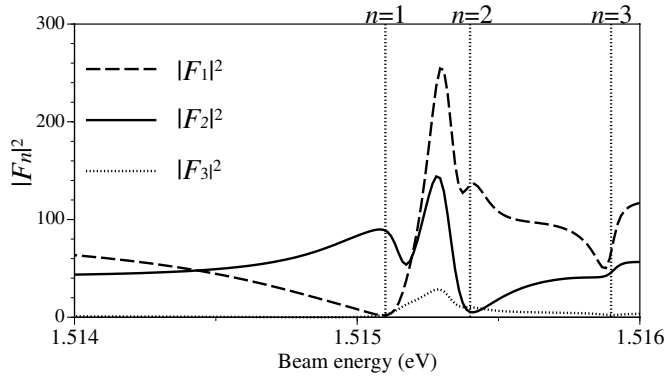

FIG. 4. Energy dependence of $|F_n|^2$ for $L = 110$ nm. The vertical dotted lines indicate the quantized excitonic levels.

this thickness. This effect causes the large nonlinear signal due to the double resonance in the susceptibility poles and the internal field. On the other hand, the separation between the peak of $|F_1|^2$ and the lowest one-exciton level is almost twice that for the $n = 2$ exciton state. Since this separation appears as the third power in the energy denominator of $\chi^{(3)}$, the enhancement of $|F_1|^2$ is not very effective for $L = 110$ nm, though its peak value is not so small. Actually, the enhancement does not appear around $L = 110$ nm if we deliberately neglect the contributions from the excitons with $n = 2$ and higher in the calculation of DFWM.

The above behavior of the internal field can be understood as follows: The internal field has the components with the spatial structure similar to that of the wave function of excitonic c.m. motion due to the self-consistency between the radiation and the induced polarization. Since these components have nanoscale spatial structure, a particular component shows a size-resonant enhancement at a particular thickness as a result of the nanoscale Fabry-Pérot interference of exciton polaritons. Generally, each component is enhanced at the resonance energy and includes the radiative shift. In the thickness region considered here, the radiative shift of the $n = 2$ exciton is not very large, and therefore, the enhancement of F_2 near the $n = 2$ excitonic level leads to the double resonance. On the other hand, the shift of the lowest level, which is positive for the film geometry, is larger than that of the $n = 2$ exciton, which leads to the smaller contribution to the nonlinear signal.

In conclusion, the systematic comparison between the observed DFWM signals of GaAs thin layers and the corresponding theoretical results has provided a decisive confirmation of the nonlocality-induced size-resonant enhancement of the nonlinear response where the nondipole type excitonic state dominantly contributes. Also the verification using the different type of material (with the small Δ_{LT}) than that assumed in the previous theoretical demonstrations (with the large Δ_{LT}) has provided an understanding of the generality of this new type of size dependence of the nonlinear response which is beyond the effect described by the macroscopic response theory. We hope that further investigation of nonlinear response in the size regime beyond the LWA will reveal the novel physics emerging from the nonlocal coupling scheme between the radiation and matter.

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[1] T. Takagahara, Phys. Rev. B **36**, 9293 (1987).
[2] Y. Kayanuma, Phys. Rev. B **38**, 9797 (1988).
[3] E. Hanamura, Solid State Commun. **62**, 465 (1987); Phys. Rev. B **37**, 1273 (1988).
[4] T. Takagahara, Phys. Rev. B **39**, 10 206 (1989).
[5] H. Ishihara and K. Cho, Phys. Rev. B **53**, 15 823 (1996).
[6] H. Ishihara, T. Amakata, and K. Cho, Phys. Rev. B **65**, 035305 (2002).
[7] K. Akiyama, N. Tomita, Y. Nomura, and T. Isu, Appl. Phys. Lett. **75**, 475 (1999).
[8] J. J. Hopfield and D. G. Thomas, Phys. Rev. **132**, 563 (1963).
[9] K. Cho and H. Ishihara, J. Phys. Soc. Jpn. **59**, 754 (1990).
[10] K. Cho, A. D'Andrea, R. Del Sole, and H. Ishihara, J. Phys. Soc. Jpn. **59**, 1853 (1990).
[11] H. Wang, K. Ferrio, D. G. Steel, Y. Hu, R. Binder, and S. Koch, Phys. Rev. Lett. **71**, 1261 (1993).
[12] Th. Östreich, K. Schönhammer, and L. J. Sham, Phys. Rev. Lett. **74**, 4698 (1995).
[13] V. M. Axt, G. Bartels, and A. Stahl, Phys. Rev. Lett. **76**, 2543 (1996).
[14] H. Ishihara and K. Cho, Phys. Rev. B **42**, 1724 (1990).
[15] H. Ishihara and K. Cho, J. Nonlinear Opt. Phys. **1**, 287 (1991).
[16] H. Ishihara and K. Cho, Phys. Rev. B **48**, 7960 (1993).