Interchange of the Quantum States of Confined Excitons Caused by Radiative Corrections in CuCl Films

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The energy states of a particle confined in a narrow space are discrete and lined up in the order of $n = 1, 2, 3, \ldots$. However, if the particle interacts with a radiation field, modification of the energy, referred to radiative correction, will occur and quantum states are expected to interchange. We investigated the center-of-mass confinement of excitons in CuCl films by a new method based on "nondegenerate two-photon excitation scattering." The energies of confined excitons in a 19.3 nm thick film are found to be lined up in the order of $n = 1, 3, 5$, because the radiative correction is very weak. On the other hand, in a 35.3 nm thick film, in which the radiative correction becomes large, the energies of quantum states are ordered $n = 2, 3, 4, 1, 5, 7$. This interchange is confirmed by comparing the calculated scattering spectra, in which radiative correction is taken into account, with the measured ones.

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Quantum confinement effects have been studied extensively over the past few decades. When a particle is confined in a narrow space, its wave function will be modified and its energy becomes discrete. This behavior has been reported in quantum wells [1], wires [2], and dots [3] of semiconductors. These phenomena are explained based on separate confinement of electrons and holes. In other words, the electrons and holes are quantized, respectively, in different subbands, and excitons are formed between quantized electron and hole levels. In this case, the excitonic and intersubband transitions are allowed only for the same quantum numbers ($n_e = n_h$) of the electron (n_e) and the hole (n_h). These quantized states are in the order of $n = 1, 2, 3, \ldots$ from lower to higher energies. This concept holds when the exciton Bohr radius is larger than the size of the quantum structure. On the other hand, when the exciton Bohr radius is smaller than the size of the quantum structure, the center-of-mass quantization of excitons will take place. CuCl Z_3-1s excitons have a small Bohr radius (~ 0.7 nm) and are a good candidate for studying center-of-mass confinement. Tang *et al.* [4] observed confined exciton states in CuCl thin films (thickness ≤ 15.7 nm), and analyzed the absorption spectra of excitons based on a long-wavelength approximation (LWA). They concluded that the confined exciton states of odd quantum numbers $n = 1, 3, 5, \ldots$ with specific wave number $k = n\pi/a$ are one-photon allowed. Here a is the film thickness.

Because of their polarization characteristics, excitons are modified due to the radiative corrections originated from their interaction with a radiative field. In a bulk crystal, these corrections cause formation of polaritons. Here, the radiative correction itself is a typical concept known, for example, as Lamb shift in atomic systems. However, differing to the atomic systems, radiative correction in excitonic systems is very large [5]. Moreover, as the sample thickness is increased, the energy shift caused by the radiative correction will become larger than the energy separation between neighboring quantum states, and the sign of the shift changes at a critical thickness when the LWA is not satisfied. Therefore, phenomena such as double resonances and interchanges of quantum states [6] are expected. Experimental observation of the interchange, however, have not been reported yet.

Conventional one-photon transmittance spectroscopy is suitable for investigating confined exciton states only when the film thickness is small. In the center-of-mass confinement regime and when the film thickness is small (15.7 nm), absorption due to quantized excitons is known to lead to dips in transmittance spectra [4]. However, in the larger thickness sample (48 nm), there is no simple correlation between the structures appearing in transmittance and the quantum states [7]. The transmission structure was interpreted as the effect of either interference between the upper-branch polariton (UBP) and the lower-branch polariton (LBP) using Pekar's ABC theory [7,8] or, more specifically, interference between the incident field caused by the background part of polarization and the radiation field caused by induced polarization using ABC-free theory [7,9]. Because of such interference effects, it is difficult to obtain accurate information on exciton states and to observe interchange from one-photon

transmittance spectra. The following discussion is based on the *ABC*-free theory.

It is thus necessary to separate the real absorption due to excitons and the interference from each other in order to characterize accurately the properties of quantized excitons. Two-photon spectroscopy is a useful method of studying confined excitons because the incident photon energy is far away from that of the exciton. In this case, the interference effects can be avoided. In this Letter, we developed a new technique, "nondegenerate two-photon excitation scattering," by which the scattering intensity of the sum frequency from the excitons excited by two lasers with different wavelengths was investigated. By using this method, we were able to observe the interchange of quantum states of confined excitons in CuCl films.

CuCl films with (111) orientations were grown on MgO (001) substrates by molecular beam epitaxy [10]. The thickness of the CuCl films were estimated from the growth rate and the measurement using atomic force microscopy (AFM). Experiments were also performed using a CuCl single crystal grown by the vapor growth technique. The sample was simultaneously excited by the 1064 nm line, the fundamental light of an Nd:YAG laser, and the light of a dye laser excited by the 532 nm line of the second harmonic of the same Nd:YAG laser. The sum of the excitation average power on the sample was 4 mW/mm^2. The pulse width and repetition rate were 15 ns and 50 Hz, respectively. A dye laser of rhodamine 610 in ethanol was scanned from 600 to 612 nm. If the sum energy of the photons from the two lasers resonates with the Z_3-1s exciton energy of CuCl, excitons will be generated. Photons with the same energy will be generated due to exciton recombination and be scattered from the sample. The scattered light was dispersed with a 32 cm single spectrometer and detected using a liquid nitrogen-cooled CCD. The measurement was performed in a backward scattering configuration. The temperature of the sample was 10 K. For comparison, transmission spectra were also measured under normal incidence using a tungsten lamp. The absorption spectrum was calculated from the minus logarithm of the transmission.

The scattering spectra of a few CuCl films and the bulk crystal obtained under nondegenerate two-photon excitation are shown in Fig. 1 along with absorption spectra. In the bulk crystal, absorption and two-photon scattering spectra are completely different. Two-photon signals were observed between the longitudinal exciton (E_L) and UBP, and there is no signal from LBP around the transverse exciton (E_T). Because of the momentum conservation law, two-photon transition is always forbidden for LBP, but allowed for UBP and longitudinal excitons [11]. Therefore, the two-photon spectrum is different from the absorption spectrum because the latter is probing LBP.

Two-photon transition may become allowed even for LBP when the film thickness is small enough. As shown in Fig. 1, the two-photon spectrum of a film with a thickness of $a = 19.3$ nm is very similar to the absorption spectrum. This is due to the relaxation of a momentum conservation law in thin films. Because of the spatial localization, the momentum of the exciton is allowed in a wider range based on the uncertainty principle. Consequently, transitions for LBP become two-photon allowed. For this film thickness, we can use LWA to describe the absorption spectrum [4]. A comparison of the absorption and two-photon spectra shows that these peaks correspond to the quantum states of confined excitons.

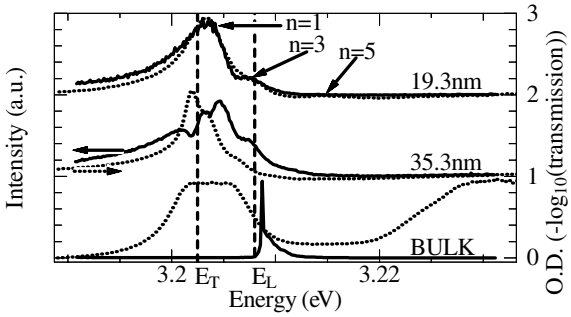

FIG. 1. Two-photon scattering spectra (solid curves) and one-photon absorption spectra (dotted curves) of bulk, 35.3 nm thick and 19.3 nm thick CuCl films at 10 K. The energy positions of E_T and E_L are transverse and longitudinal excitons. In the case of a film thickness of 19.3 nm, the two-photon spectrum is almost the same as the one-photon spectrum, and transitions associated with quantum states of $n = 1, 3, 5$ were observed. When the film thickness was increased to 35.5 nm or more, however, the two-photon spectrum is greatly different from the one-photon spectrum.

As shown above, two-photon spectra probe different exciton states in a bulk but the same exciton states in a thin film compared with one-photon spectra. It is thus interesting to examine the case of intermediate film thickness. As shown in Fig. 1 for a film thickness of 35.3 nm, the difference of these two spectra is an intermediate degree. This difference indicates that absorption spectroscopy cannot accurately probe the quantum states of confined excitons due to the influence of interference of the incident light.

Now, we adopt a theoretical approach to interpret the results. We consider the dependence of the energy on film thickness after taking into account the radiative correction. Such dependence of the confined excitons for $n = 1$ in CuCl films [12] and for $n = 1, 2$ in GaAs quantum wells [5] has been reported previously. Here, we calculate the radiative correction up to $n = 7$ based on the equation

$$U_n = i \iint_0^a \psi_n(x_i)\psi_n(x_j) \exp[ik_{\omega_3}|x_j - x_i|]\, dx_i\, dx_j.$$

The excitons, described by the wave function of $\psi_n(x_i)$ at the position x_i, are considered as oscillators emitting the radiation with a single frequency. This radiation propagates and creates an electric field inside the film, which further interacts with itself at the position x_j and modifies

its energy. This modification is generally a complex value and can be written as $U_n = R_n + i\Gamma_n$. The real part R_n represents the energy shift and the imaginary part Γ_n is proportional to the reciprocal of the radiative lifetime. Therefore, the energy levels of confined excitons are written as $E_n = E_g - E_{\mathrm{ex}} + \{\hbar^2/[2(m_e + m_h)]\}[(n\pi)/a]^2 + R_n$, where E_g is the band gap of CuCl, E_{ex} is the Z_3-1s exciton binding energy, and m_e and m_h are effective masses of electrons and holes, respectively. As shown in Fig. 2, an interchange of the energies of confined excitons takes place. For example, because of the positive shift of the $n = 1$ state [6], the energy of this state is higher than that of the $n = 2$ state when the film thickness is larger than 15.5 nm. Here, the quantum number is named the same as that corresponding to the exciton modes before modification.

The two-photon excitation scattering spectra is calculated by the probabilities of exciton generation, exciton recombination, and exciton existence. The last term is calculated using a Lorentzian function including E_n and Γ_n. In addition, when we compare the calculation with experimental spectrum, we take into account all possible interactions among quantum states and the fano effect [13], which makes the spectrum slightly asymmetric. For simplicity, we make some assumptions. The wave number of the light is assumed to be constant in the measured range. The wave function of excitons is assumed to be a sine function, because the effect of the dead layer is negligible [8].

The calculated results are shown in Figs. 3(a)–3(c) together with that of measured results. The lower part shows the experimental spectra and the upper part shows the calculated ones. Figure 3(a) shows that the measured spectra for $a = 19.3$ nm correspond well to the calculated results for $a = 16.5$ nm. Figure 3(b) shows that the measured spectra for $a = 27.0$ nm correspond well to the calculated results for $a = 26.6$ nm, and Fig. 3(c) shows that the measured spectra for $a = 35.3$ nm correspond well to the calculated results for $a = 29.1$ nm. The mismatch in film thickness may come from errors in the measurement of the growth rate.

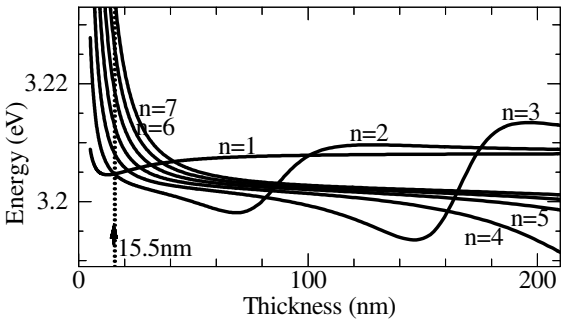

FIG. 2. Calculated energy levels of confined excitons after including radiative corrections. The energy of the quantum number $n = 1$ is crossing that of $n = 2$ at 15.5 nm due to radiative corrections.

The dotted curves in Figs. 3 show the components of every quantum state. The spectra of $a = 19.3$ nm were found to be constructed only from odd states $n = 1, 3, 5, \ldots$ with no contribution from even states $n = 2, 4, 6, \ldots$. This result is similar to that obtained under LWA [4]. On the other hand, in the case of the film with a thickness of 35.3 nm, the spectra were found to be constructed from not only odd states but also even states. The phase of even states is inverse to that of odd states, so even states appear as dips in the strong and broad $n = 1$ peak. Moreover, the energies of these states are apparently in the order of $n = 2, 3, 4, 1, 5, 7$. This reordering just comes from the radiative correction. In the case of a film with an intermediate thickness of 27.0 nm, the observed quantum states are ordered as $n = 2, 3, 1, 5, 7$, which is an intermediate situation.

The calculated spectra agree well with the measured ones. In this calculation, we used the following parameters: dielectric constant $\epsilon_\infty = 5.59$ [14], refractive index $n = 1.97$ for 610 nm and $n = 1.92$ [15] for 1064 nm, exciton effective mass $M = 2.3m_0$ [14], longitudinal

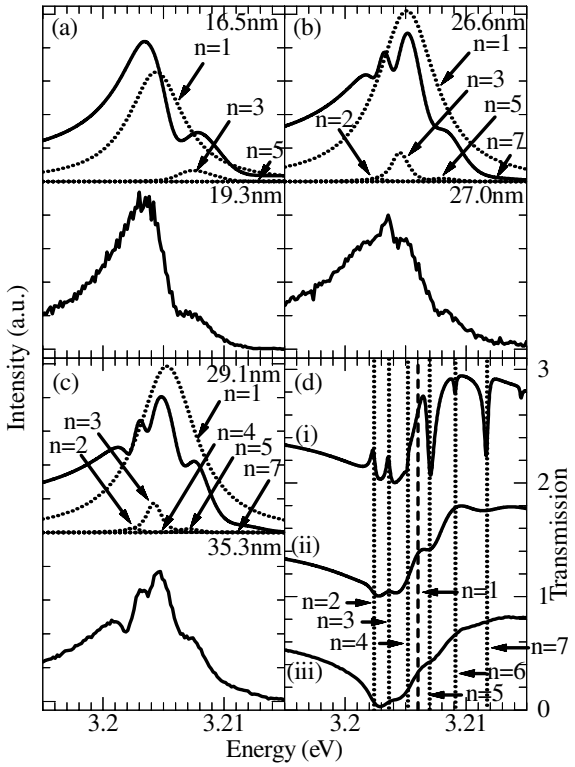

FIG. 3. (a)–(c) Measured (lower) and calculated (upper) two-photon scattering spectra of CuCl films with different thicknesses. The calculated components of individual quantum states are shown by dotted curves, and the total calculated scattering spectra are shown by solid curves. (d) Curves (i) and (ii) are calculated transmission spectra for a thickness of 29.1 nm using nonradiative damping 0.1 and 0.4 meV, respectively. (iii) The measured transmission spectrum for 35.3 nm. Even if nonradiative damping is very small, we cannot identify the position of $n = 1$ in the transmission spectrum.

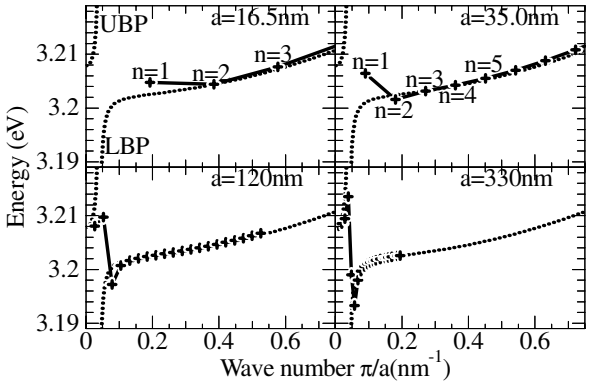

FIG. 4. Energy vs wave number of confined excitons for films of various thicknesses. The wave number was calculated by $n\pi/a$. In the film thickness $a = 16.5$ nm, the energy of the $n = 1$ state is higher than that of $n = 2$, and, in the film thickness $a = 35.0$ nm, the energy of $n = 1$ is higher than that of $n = 4$. As the film thickness is increased further to $a =$ 120 nm, the $n = 2$ state pops to higher energy also. In the case of $a = 330$ nm, $n = 1, 2, 3, 4$ states keep higher energies and become close to UBP.

exciton $E_L = 3.2079$ eV [16] and transverse exciton $E_T = 3.2022$ eV [16], and nonradiative damping factor of 0.4 meV. The calculation was broadened by assuming a Gaussian fluctuation of 5% in film thickness.

Transmittance spectra are calculated using *ABC*-free theory [7] and shown in Fig. 3(d) [(i) and (ii) along with experimental result (iii)]. A very good agreement between calculated and measured spectra is obtained when the nonradiative damping is 0.4 meV. If we consider the case of very small damping 0.1 meV, the peaks of transmittance spectra appear at the energy positions of the quantum state $n = 2, 3$ and dips appear at \those of quantum states $n = 5, 6, 7$. However, the quantum state $n = 1$ appears as neither a peak nor a dip. This is because the broad structure of the $n = 1$ state is buried in the interference structures coming from the superimposed field of the scattered and incident fields. Consequently, we cannot identify the energy of quantum state $n = 1$ from transmittance spectra, even if the sample has very high quality and the nonradiative damping is very small.

Interchange is easily understood by inquiring into the dependence of exciton energy on the wave number $(n\pi/a)$. The results for a few films are shown in Fig. 4. In the case of a very thin film (16.5 nm) where the radiative correction is small, the quantum states are ordered as $n = 2, 1, 3, \ldots$. However, in a relatively thick sample (35.0 nm) where the radiative correction is larger, the energy of the $n = 1$ quantum state has a large energy shift and becomes higher than that of $n = 4$. As the film thickness is increased further to 120 nm, the energy of the $n = 2$ state pops to higher energy also. We noted that the popping occurs when $2a/n$ is the same order as its radiation wavelength. Finally, in the case of $a = 330$ nm, $n = 1$ and $n = 2$ states converge to the energy of longitudinal excitons. Since the interaction length of an exciton and radiation determines the interaction strength, the popping height is related to film thickness a. In the infinity limit of the film thickness, these quantum states pop from 0 to infinity. This behavior agrees with UBP or LBP of the bulk polariton.

In summary, we have developed a new technique and observed purely confined exciton states. We were also able to observe interchange of exciton quantum states originating from radiative corrections. Our results shed light on the physical nature of excitons in the center-of-mass confinement regime.

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