Multiple light-coupling modes of confined excitons observable in photoluminescence spectra of high-quality CuCl thin films

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We report the observation of multiple light-coupling modes of excitons confined in CuCl thin films with thicknesses of a few hundred nanometers beyond the long-wavelength approximation in photoluminescence spectra. Due to a remarkably long coupling length between light and multinode-type excitons resulted from very high crystalline quality of thin films, photoluminescence signals from the excitonic states corresponding to not only odd but also even quantum numbers, which are optically forbidden in the long-wavelength approximation, are clearly observed. The full width at half maximum of the excitonic state deduced qualitatively from the corresponding photoluminescence band shows almost the same dependence on the quantum number as the theoretical prediction.

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I. INTRODUCTION

Quantum confinement effects of excitons in semiconductor systems with reduced dimensions have attracted considerable attention because of their potential applications to nonlinear optical devices, and as a means of exploring the basic physics of the quantized excitonic states.[1] In a strong confinement regime, where the exciton Bohr radius is larger than the size of the nanostructure, the electrons and holes are individually confined leading to quantization of their energy levels in different subbands. Excitons then are formed between quantized electron and hole levels. The excitonic transitions are optically allowed for the same quantum numbers ($n_e = n_h$) of the electron (n_e) and the hole (n_h).[2] On the other hand, in a weak confinement, where the exciton Bohr radius is smaller than the size of the nanostructure, the picture of the confinement of the excitonic center of mass (c.m.) motion is suitable for investigating the optical processes. In the framework of the long-wavelength approximation (LWA), wherein the spatial structure of the light wave is neglected by assuming a much longer light wavelength than the excitonic coherent length, excitonic transitions obey the parity selection rule that only the excitons with odd-parity wave functions are optically allowed and the lowest state is most strongly coupled with light.[3] Under this framework, the light-matter interaction is size-linearly enhanced and then saturated by the excitonic coherent length, because of the violation of c.m. confinement due to the dephasing, or by the wavelength of the resonant light, because of the phase mismatch between the lowest optically allowed exciton and the light wave.[4,5] However, the coherent length of the exciton state can be very long in adequately high quality nanostructures. In this case, the spatial structures of the light can be no longer neglected leading to consequently the breakdown of the LWA.[6]

A peculiar nonlinear response contradicting the LWA was reported in GaAs thin film, wherein the size resonant enhancement of the nonlinear signal arises from the nondipole-type excitonic state, which is normally an optically forbidden state.[7,8] By using a method based on nondegenerate two-photon excitation scattering, Syouji *et al.* observed successfully the purely confined excitonic states with not only odd but also even quantum numbers from CuCl thin films.[9] Recently, our group has observed experimentally a remarkably strong coupling between light and exciton in high quality CuCl thin films with thicknesses of several hundreds of nanometers as an exceptionally short radiative decay time reaching 100 fs,[10] which is several orders of magnitude shorter than the typical excitonic nonradiative decay time.[11] The results of theoretical analysis demonstrate that the coupling between the light wave and the extended multinode-type excitonic wave over several wavelengths is formed as long as the wave function of the c.m. motion of exciton is coherently extended over the whole volume of a system.[12,13] In a thin film with very high crystalline quality, the size-dependent increase in the light-matter interaction is no longer limited by the light wavelength and the radiative decay rate is enhanced in a larger system than nanostructures with adequately improved crystalline quality.

In the non-LWA regime, linear optical spectroscopy such as transmittance and reflectance spectroscopy exhibits complicated interference effects between the incident and the scattering fields, and we find that the energies of confined excitons coincide with the peak or dip structures in the spectra if their radiative coupling is not strong.[14,15] However, the quantum levels of lower-numbered states with a strong radiative coupling are largely shifted from such peak or dip structures, and do not appear in those spectra.[16] Thus, nonlinear methods such as degenerate four-wave mixing (DFWM) and nondegenerate two-photon excitation scattering spectroscopy were used to examine the quantum states of confined excitons.[8–10]

In this paper, we show the experimental evidence that the excitonic states in CuCl thin films, both lower and higher, even and odd quantum numbers, can be observed obviously even by a simple incoherent spectroscopy, namely photoluminescence (PL), provided that the crystalline quality is sufficiently high.

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By changing the excitation condition from the resonant to band-to-band excitations, the observed mode structures in the PL spectra are confirmed reasonably to originate from the luminescence of the exciton states, not from the resonant scattered one, which is owing to their ultrafast nature in the radiative decay. Based on the qualitative fittings of the PL spectra, the full width at half maximum (FWHM) of the excitonic states can be received and they show the same dependence on the quantum numbers as predicted by the theoretical calculation for all kinds of the excitation conditions. This result indicates that high coherence of matter systems is clearly reflected even in its incoherent photon-processes, which reveals unexploited potentials of the PL spectroscopy.

II. EXPERIMENTAL PROCEDURES

CuCl thin films were grown by means of the molecular beam epitaxy (MBE) method. Crystalline quality of the CuCl films was extremely improved by our novel technique of electron beam irradiation at the beginning of MBE growth,[17] and experiments using high quality thin films with very small dephasing constants (Γ) of about 0.2 meV can be feasibly realized. The grown films were mounted in a helium flow cryostat and the temperature was cooled below 10 K. DFWM spectra were measured using the second harmonic of a mode-locked Ti:sapphire laser, whose repetition rate and pulse duration were 80 MHz and 110 fs, respectively. Photon energy of the pulse was tuned to approximately the transverse exciton energy. The excitation light was split into two pulses and both of them were focused to the same spot on the sample surface. Polarizations of two pulses were parallel and the delay time was set to zero. PL spectra were detected in a forward configuration. Three other excitation sources were used for different excitation conditions as follows. The second harmonics of two other mode-locked Ti:sapphire lasers with pulse durations about 100 fs and 1 ps were used for the biexciton resonant excitation, while a cw He-Cd laser with a excitation energy of 3.81 eV was utilized for the band-to-band excitation. All the excitation lights were directed to the same position on the sample surface as in the DFWM measurement. To remove efficiently the scattering light of the excitations in the PL spectra, two polarizers with crossing polarizations were used. One was located on the excitation beam path just before the focusing lens, another was placed between two lens, collimating and focusing ones, in the PL detecting system. The PL signal then was transmitted through an optical fiber to a 50-cm monochromator equipped with a nitrogen-cooled CCD. The spectral resolution was better than 0.08 meV. Film thickness and Γ at the measured spot were derived by fitting to the reflection spectra measured using the same geometry and excitation light as those in the measurement of DFWM.

III. RESULTS AND DISCUSSION

A typical reflection spectrum of a high quality CuCl thin film measured with an incident light nearly perpendicular to the film surface is displayed in Fig. 1. The experimental data show a good agreement in the excitonic energy region with the theoretical calculation assumed for a small nonradiative

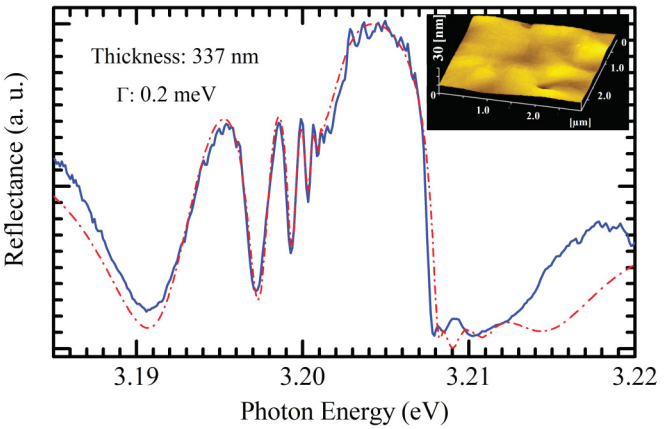

FIG. 1. (Color online) A typical reflection spectra of a CuCl thin film (solid line) measured in the excitonic energy region at the same excitation spot as in the degenerate four-wave mixing and photoluminescence measurements. The dashed-dot line is the theoretically calculated fitting curve assumed for a dephasing constant Γ of 0.2 meV and a film thickness of 337 nm. The inset show the corresponding atomic force microscope image scanned over an area of 3 μm $\times$ 3 μm on the sample surface with a vertical scale of 30 nm.

dephasing constant Γ of 0.2 meV and a thickness of 337 nm. This value of the dephasing constant is rather smaller than that of samples used in the previous reports.[9,15,18] We also checked for the thin film morphology irradiated with a 5-keV electron beam by means of an atomic force microscope (AFM). The inset displays the corresponding AFM image of the thin film surface scanned over a surface area of 3 μm $\times$ 3 μm. The roughness of the thin film at a flat region is estimated to be about 1-4 nm. It is obvious that the thin film quality as well as its surface condition is extremely improved than the previous reports due to an appropriate irradiation on the CaF_2 buffer layer, just before the CuCl growth, of the electron beam. The accelerated electrons remove the F^- ions locating near the CaF_2 buffer layer's surface, the empty positions left by the F^- ions then will be filled up by Cl^- ions during the growth of CuCl layer. These replacements result in a better wettability between the CaF_2 buffer layer and the subsequently grown CuCl layer leading to a great improvement of the CuCl thin film quality and morphology.[19,20] The detailed examination of the effects of the electron beam irradiation including the electron flux rate, total number of irradiated electrons, etc. on the film quality and surface will be published elsewhere soon. In the non-LWA regime, the sample quality takes a key role in determining and realizing a harmonized coupling between the light and the multimode-type excitonic waves.[10] A high quality thin film increases subsequently the possibility for observation of a PL spectrum with obvious, separated excitonic mode structures as discussed in the following.

Figure 2(a) shows the DFWM as well as the PL spectra measured under various excitation conditions including an excitonic resonant fs-pulsed excitation (the excitation energy of 3.202 eV), biexciton resonant fs-pulsed excitation, ps-pulsed excitations (the excitation energy of 3.186 eV), and a band-to-band cw excitation (the excitation energy of 3.81 eV), of the CuCl thin film with a thickness of 325 nm and a dephasing constant Γ of 0.2 meV derived from fitting of the

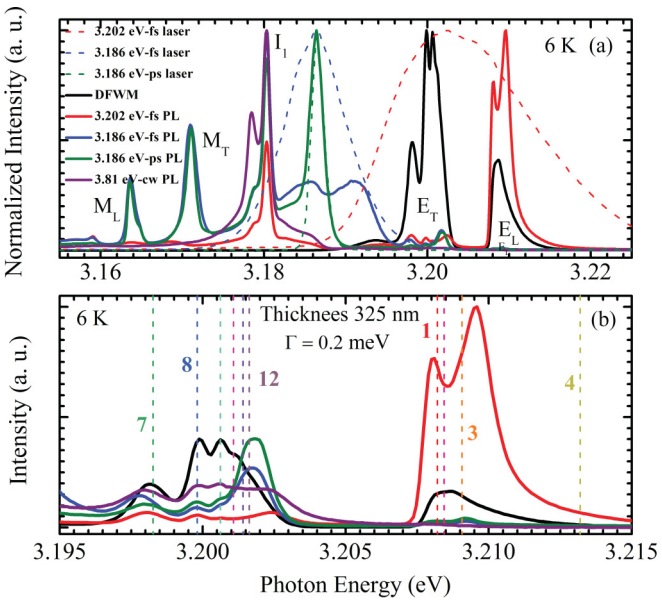

FIG. 2. (Color online) (a) The degenerate four-wave mixing spectrum as well as the photoluminescence spectra measured under various kinds of the excitation conditions (colored solid lines) for a CuCl thin film with a thickness of 325 nm and a dephasing constant Γ of 0.2 meV at 6 K. The M_L and M_T bands are the biexciton luminescence resulting from radiative relaxation of excited biexcitons to the longitudinal (E_L) and transverse (E_T) excitonic states, respectively. The I_1 band is originated from excitons bound to neutral donors. The dashed lines indicate the different excitation lasers. (b) The degenerate four-wave mixing and photoluminescence spectra expanded in the excitonic energy region. The spectra are multiplied by suitable factors for an easy comparison of the detailed mode structures in the degenerate four-wave mixing and photoluminescence spectra. The theoretical calculations of the energies of excitonic states with different quantum numbers for the film thickness of 325 nm are indicated by the dashed lines.

reflection spectrum at 6 K. The measured DFWM spectrum exhibits several peaks, which have never been observed in samples grown by traditional methods. As examined previously for various thicknesses of CuCl thin films,[10,18] the peak photon energies shown in the DFWM spectrum again coincide consistently with the theoretically calculated eigenenergies of the excitonic states indicated by the dashed lines in Fig. 2(b). It is interesting that the same mode structures as observed in the DFWM spectrum appear obviously in the PL spectra measured under both the resonant and band-to-band excitation conditions. One might think a possibility of the resonant signal scattered from the quantized excitonic levels instead of the excitonic luminescence under the resonant excitations. However, the observation of the same mode structures in the PL spectrum measured under the band-to-band excitation whose photon energy is far away from the excitonic energy levels directly denies the possibility of the scattered signal. Just after a band-to-band excitation, hot electrons and holes are created individually. The excessive energies of electrons and holes then will be dissipated, for example by phonon interactions, and electrons and holes are finally combined to form excitons at different energy levels. In general case, due to fast nonradiative relaxations, excitons are mostly accumulated at the lowest energy level leading to a dominant luminescent band of this lowest state in PL spectra. However, in our particular situation where the radiative decay rates of high energy levels are comparable or faster than the conventional nonradiative relaxation as discussed later, the luminescent bands from these high energy levels are also possible to appear obviously in the PL spectra. Therefore, the mode structures in the PL spectrum under the band-to-band excitation should be the excitonic luminescent bands. In addition, for the biexciton resonant excitations, the integrated intensity of the excitonic emission shows a nearly quadratic dependence on the excitation power reasonably leading to the relaxation-from-biexciton origin of the observed excitons. Consequently, we conclude that the excitonic luminescence was efficiently detected under various excitation conditions. T. Mita and N. Nagasawa discussed fine structures at excitonic resonance caused by Fabry-Perot fringes in transmission and reflection spectra of a 150-nm CuCl thin film on the view point of normal polariton dispersion for bulk.[14] They successfully explained the energies of peak and dip structures in the spectra based on the interference of polaritons obeying the dispersion for bulk. However, those energies do not necessarily coincide with exciton modes with radiative correction especially for the lower-numbered states with strong radiative coupling because they locate far away from the polariton dispersion curve due to the large radiative corrections.[9,12,13]

In the PL spectra, some peaks corresponding to the excitonic states with even quantum numbers, which are optically forbidden in the LWA regime,[3] are observed. In a high quality thin film, strong couplings between the light wave and the multinode-type excitonic waves, not only oddnode-type (odd quantum numbered) but also evennode-type (even quantum numbered), are formed efficiently and result in fast radiative decay rates of the excitonic states,[10] which are much faster than the typical nonradiative dephasing rates.[11] Moreover, differently with other conventional linear spectroscopy, such as transmittance and reflectance spectroscopy, the PL spectrum is expected to not contain complicated interferences[14] due to inelastic nature of the response. For the case of excitonic resonant excitation in which there is no difference in photon energy between the excitation light and PL, the incoherent nature of PL would also prevent efficiently just mentioned interferences. As a result, the excitonic luminescence from quantum states with both odd and even quantum numbers, which could only be realized in previous works by nonlinear spectroscopy, can be efficiently obtained by simple PL spectroscopy. In both PL and DFWM spectra, the energy difference between the excitonic state of $n = 1$ and $n = 2$ is so small that the signals contributed from the excitonic state of $n = 2$ could not observe clearly. With the film thickness of 325 nm, the eigenenergy of the exciton state of $n = 6$ is theoretically calculated to be 3.1939 eV locating at the low-intensity tail of the excitation light in the DFWM measurement. Therefore, the signal from the excitonic state of $n = 6$, in fact, still could be observed in the DFWM spectra but with a rather small amplitude. In PL spectra, the luminescent band of the excitonic state of $n = 6$, for this thickness, is close to that of $n = 5$ exciton state (3.19219 eV) whose band width is predicted to be very broad. Thus, it is difficult to see the luminescent band of the excitonic state of $n = 6$ for this film thickness. However, by changing

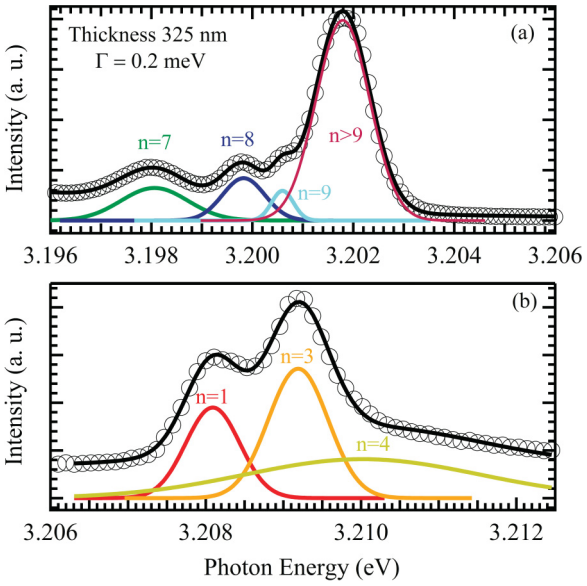

FIG. 3. (Color online) (a) The photoluminescence spectrum in the transverse excitonic energy region under the biexciton resonant ps-pulsed excitation (open circles) and the Gaussian fitting components originating from the excitonic states with the quantum numbers of n = 7,8,9 and n > 9 (colored solid lines). (b) The photoluminescence spectrum in the longitudinal excitonic energy region under the same excitation (open circles) and the Gaussian fitting components originating from the excitonic states with the quantum numbers of n = 1,3,4 (colored solid lines).

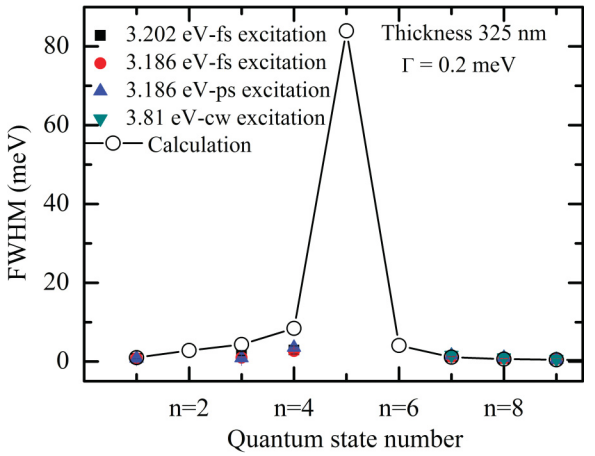

FIG. 4. (Color online) The full width at half maximum of the excitonic states extracted from the photoluminescence spectra as a function of the respective quantum number under various excitation conditions (solid squares, circles, upward and downward triangles). The theoretically calculated full width at half maximum of the excitonic states is presented by the open circles.

the film thickness, the signals of the excitonic state of n = 6 in both DFWM and PL spectra become possible to be observed obviously.

To examine characteristics of each excitonic state, it is necessary to identify its contribution in the detected PL spectra. Figures 3(a) and 3(b) show the PL spectra under the biexciton resonant ps-pulsed excitation and the typical fitting curves composed of several Gaussian components around the excitonic transverse and longitudinal energies, respectively. In the fitting process, the overlap of the excited excitonic states with the quantum numbers larger than 9 is assumed to form a spectrally broad Gaussian component. The other Gaussian fitting components are attributed to the excitonic states with different quantum numbers denoted nearby the fitting components. For all different excitation conditions, such a kind of the fitting process qualitatively reconstructs the measured PL spectra. The corresponding FWHM of each excitonic state could be consequently deduced. Figure 4 shows the FWHM of the excitonic state as a function of the quantum number for various kinds of the excitation conditions. These broad FWHM of the excitonic states are much larger than the dephasing damping constant Γ = 0.2 meV received from the reflection spectrum and consistent qualitatively with our recent report wherein the radiative decay time, which is inversely proportional to the FWHM of the excitonic state, reaches the order of 100 fs, much faster than conventional excitonic dephasing processes.[10,18] No noticeable differences in the FWHM of the same excitonic state are observed with different excitation conditions. In PL spectroscopy, the spectral width of a luminescent band from an excitonic state is determined primarily by the natural characteristics of the state itself not by the excitation condition which generally causes different rise times in time-resolved spectroscopy. The theoretical calculation of the FWHM of the excitonic state caused only by radiative processes is also presented in Fig. 4 by open circles as a function of the quantum state number. For the examined film thickness, the theoretical calculation predicts the strongest harmonic coupling between the light wave and the excitonic wave with the quantum number of 5 leading to a very broad FWHM of ~80 meV.[12] Due to such a broad spectral width, the luminescent contribution from the excitonic state with the quantum number of 5 is difficult to be extracted from the measured PL spectra. For the excitonic states with other quantum numbers, the experimentally obtained FWHM shows the same tendency on the quantum number as the theoretical calculation but with smaller values for small quantum numbers such as n = 3,4. Around the transverse excitonic energy region, the luminescent bands originated from the excitonic states with the quantum state numbers of 7, 8, and 9 are spectrally well separated due to noticeable energy disparities of a few meV leading to an appropriate estimation of the FWHM of each luminescent band. As a result, the FWHM of these excitonic states almost coincide with the theoretical calculation. On the other hand, a considerable overlap between the rather broad luminescent band from the excitonic state with the quantum number n = 4 and that from the excitonic state with the quantum number n = 3 might lead to an unintentional underestimation of the FWHM of these states in comparison with that predicted by the theoretical calculation.

IV. CONCLUSION

In conclusion, we have shown that if very high quality thin films are prepared successfully, due to a remarkably long coupling length between light and multinode-type excitons, the radiative decay rates of excitonic states even for which locating at high energy levels exceed the nonradiative decay

rates because of the ultrafast nature of their radiative processes, which leads to an obvious observation of many excitonic luminescent bands in PL spectra. In this particular situation, the radiative recombination is expected to be still efficient even at high temperatures, therefore, in future, temperature dependent PL spectra might help us to retrieve more useful information for further confirmation of our recent results obtained by means of DFWM spectroscopy.[21]

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