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Efficient radiative recombination of multinode-type excitons up to room temperature in CuCl thin films

M. Ichimiya [a,b,*], K. Mochizuki [b], M. Ashida [b], H. Yasuda [c], H. Ishihara [c], T. Itoh [b]

[a] Department of Physics, Osaka Dental University, Hirakata, Osaka 573-1121, Japan
[b] Department of Materials Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan
[c] Department of Physics and Electronics, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan

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ABSTRACT

We report the observation of anomalous temperature dependences of degenerate four-wave mixing spectra in CuCl thin films with high crystalline quality. The observed temperature dependence is in good agreement with the phase-decay-constant dependence of calculated induced-polarization spectrum. An excitonic state with large radiative width can be observed at high temperatures as superradiance is faster than the dephasing process. We succeeded in observing the DFWM signal up to room temperature based on the extremely large radiative width peculiar to the thickness region beyond the long-wavelength approximation regime.

1. Introduction

High-speed and efficient responses are essential for the realization of high-performance all-optical switching devices, while the realization of a system that combines both of them has been very difficult because resonant excitation necessary for large nonlinearity usually causes long radiative decay time due to the long lifetime of excitons. Nanostructures have attracted much attention as one of the promising candidates for realizing ultrafast nonlinear optical response, where polarization waves are confined and the spatial structure of a light wave is neglected as illustrated in Fig. 1(a). In this long-wavelength approximation (LWA) regime, only the excitons with odd-parity wave functions are optically permitted and the lowest state (white line) is most strongly coupled with light as illustrated by a right schematic spectrum (black line). Under this framework, characteristic effects such as size-dependent quantized spectrum [1] and size-linear increase in light–matter interaction volume leading to an enhancement of radiative decay rate, i.e. superradiance, appear [2–4], while increase in light–matter coupling is believed to be saturated up to the size region where the spatial structure of the internal field should be taken into consideration. On the other hand, a remarkably strong coupling between light and an exciton is observed in high-quality CuCl thin films with a thickness of several hundred nanometers and an exceptionally short radiative decay time reaching 100 fs [5], which is several orders of magnitude shorter than the typical excitonic radiative decay time. 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 illustrated in Fig. 1(b) as long as wave functions of the center-of-mass motion of excitons are coherently extended to the whole volume of a system [6]. In this regime, $n \geq 2$ excitons can interact with light and the excitonic state whose wave function is the most matched with that of the light wave is replaced in turn depending on the system size. In thin films with very high crystalline quality, size-dependent increase in light–matter interaction volume is no longer limited by the light wavelength, and the radiative decay rate is unlimitedly enhanced in a system larger than nanostructures with adequately improved crystalline quality.

Wide-gap semiconductor CuCl is a candidate for highly efficient optical devices in the ultraviolet region because of much stronger radiative coupling per unit cell volume [7] and large exciton binding energy (about 200 meV). The main reason why it has never been utilized except for basic research at low temperatures is the low radiative decay rate around room temperature due to dephasing of excitons by interaction with optical phonons. However, the ultrashort radiative decay time observed in high-quality thin films is significantly less than the excitonic dephasing time, which is normally in the order of picoseconds [8,9]. This interchange would lead to an unconventional situation where the coherent optical response is completed before the excitation is affected by phase decay. That is, in this inverted situation, the efficiency of radiative decay peculiar to CuCl would be maintained even at high temperatures. In the present work, we experimentally demonstrate an anomalous temperature dependence of nonlinear optical response associated

* Corresponding author at: Department of Physics, Osaka Dental University, Hirakata, Osaka 573-1121, Japan. Tel.: +81 72 864 3061.
E-mail address: ichimiya@cc.osaka-dent.ac.jp (M. Ichimiya).

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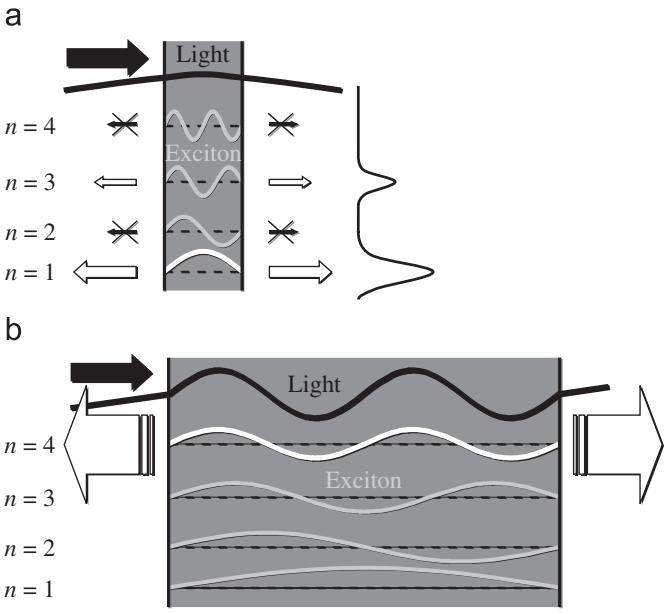

Fig. 1. Images of coupling between light and excitons in the LWA regime (a) and harmonized wave–wave coupling between a multinode-type exciton and light (b). The black curve on the right in (a) is a schematic spectrum. The states most strongly coupled with the light field are indicated in white. In the case of the illustration in (b), the $n=4$ exciton is most strongly coupled with light and the range of phase matching reaches a couple of wavelengths of light.

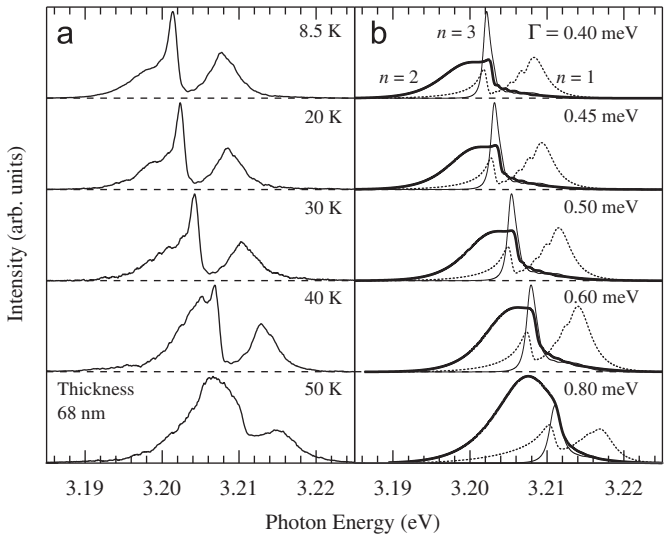

Fig. 2. (a) DFWM spectra for several temperatures in a high-quality CuCl thin film with a thickness of 68 nm. (b) Induced-polarization spectra for several phase decay constants. The parameters representative of CuCl are used and the film thickness is 68 nm. For comparison with the measured spectra, photon energy of each spectrum is modified depending on energy shift by the thermal effect at corresponding temperature. The shift energy is determined from fitting of the measured reflection spectrum.

with ultrafast radiative decay using high-quality CuCl thin films with thicknesses beyond the LWA regime.

2. Experimental procedures

CuCl thin films were grown by means of the molecular beam epitaxy (MBE) method [10]. Crystalline quality of the CuCl films was much improved by our novel technique of electron beam irradiation at the beginning of MBE growth, and experiments using high-quality thin films with a very small phase decay constant (Γ) of less than 1 meV can be realized. The grown films were mounted in a helium flow cryostat and the temperature was set from 5 to 300 K. Degenerate four-wave mixing (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 at each temperature in CuCl and the spectral width was approximately 14 meV. Light was split into two pulses and both of them were focused onto the same spot on the sample surface. Polarizations of the two pulses were parallel and the delay time was set to be zero. The signal light was transmitted through an optical fiber to a monochromator equipped with a CCD. The spectral resolution was better than 0.08 meV. Film thickness, Γ at the measured spot and exciton energies at the measured temperature were derived by fitting to the reflection spectrum measured using the same geometry and excitation light as those in the measurement of DFWM.

3. Results and discussion

In order to demonstrate the abovementioned drastic situation, we observe DFWM, which is one of the standard nonlinear optical processes. DFWM spectra of a high-quality CuCl thin film for several temperatures are shown in Fig. 2(a). The three components that have never been observed in samples grown by traditional methods are observed and the intensity ratios among these components change as temperature increases. Fig. 2(b) shows the induced-polarization spectra, which are derived from the following theoretical calculations: for both frequency and time domain calculations, we solve the simultaneous equations comprising the Maxwell equation and the constitutive equation describing a non-local relationship between the induced polarization and the electric field that depends on the microscopic positions [6]. Since the self-consistency between polarization and electric field is completely considered, size-dependent radiative correction (shift and width) automatically appears in the result. The phase decay constant (Γ) is phenomenologically introduced and calculations are performed with Γ. Shapes of the measured DFWM spectra closely reflect those of the calculated induced-polarization spectra. The three components in the DFWM spectrum correspond to the excitonic states for $n=1$–3. The component for the state of $n=3$ is reduced as temperature increases and is hardly observed at 50 K. On the other hand, relative intensity for the excitonic state of $n=2$ increases with temperature and becomes dominant at 50 K. Temperature dependence of the DFWM spectrum is in good agreement with Γ dependence of the induced-polarization spectrum. This result means that the phase decay rate increases with temperature and the radiative decay rate for the excitonic state of $n=2$ is considered to be still higher than the phase decay one for $\Gamma=0.80$ meV. The non-monotonic thickness dependences of calculated radiative width for each excitonic state are shown in Fig. 3. The radiative width for $n=2$ at 68 nm is 5.0 meV, which is much higher than 0.80 meV, and the smaller value of that for $n=3$ (0.30 meV) is consistent with the result of the DFWM experiment, where the component for $n=3$ rapidly decreases as temperature increases by corresponding to the change in Γ from 0.40 to 0.80 meV. The difference between radiative widths for $n=2$ and 3 is reflected in that of spectral widths for the two components in the DFWM spectrum. The calculated radiative decay time corresponds to $\hbar/2\gamma$, where γ indicates radiative width. That for the excitonic state of $n=2$ at 68 nm is estimated to be 66 fs, which