

Subpicosecond spectroscopy of the optical nonlinearities of CuCl quantum dots

K. Edamatsu, S. Iwai, and T. Itoh

Department of Applied Physics, Faculty of Engineering, Tohoku University, Sendai 980-77, Japan

S. Yano and T. Goto

Department of Physics, Faculty of Science, Tohoku University, Sendai 980-77, Japan

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We have observed of ultrafast time-resolved nonlinear optical absorption spectra of confined excitons in CuCl quantum dots embedded in a NaCl matrix. The main part of the nonlinear change consisted of blueshifts of the Z_3 and Z_{12} exciton bands, and their decay had two time constants that coincide with the luminescence lifetimes of excitons and of excitonic molecules. A microscopic mechanism for the optical nonlinearities of confined excitons is discussed.

The nonlinear optical response of mesoscopic semiconductor structures such as quantum wells, wires, and dots has attracted much attention since it would lead to the realization of new optically functional media. Microcrystals of semiconductors embedded in glassy or crystalline matrices are one realized form of mesoscopic quantum dots (QD), in which carriers and/or excitons are confined three dimensionally. In a QD, multiply created carriers and/or excitons should strongly interact with one another, thus generating large optical nonlinearity.¹⁻⁵ Therefore, for studying the mechanism of the optical nonlinearity of a QD in connection with the dynamics of excitons, time-resolved spectroscopy with response time sufficiently shorter than the excitonic lifetime is quite important.

With regard to the confinement of an exciton or an electron-hole pair in a QD, there are two extreme cases which depend on the size of excitons relative to that of the QD.^{6,7} The confinement of an exciton in a CuCl QD falls within the exciton confinement regime, in which the exciton radius is much smaller than the size of the QD. In this case, it is assumed that the internal motion of an exciton keeps most of its characteristics as in a bulk crystal. Since the excitonic properties of the bulk CuCl crystal have been extensively studied,⁸ CuCl is an ideal material for the study of excitons confined in QD's under the exciton confinement regime. Although the optical linear^{6,9,10} and nonlinear¹¹⁻¹⁵ optical responses of the confined excitons in CuCl QD have been extensively studied, time evolution of the nonlinear response has not been investigated in order to clarify the mechanism of the nonlinearity. In this paper, we present the results of subpicosecond pump-probe spectroscopy of the nonlinear optical response of CuCl QD's, and discuss the mechanism of the optical nonlinearities in connection with the dynamics of the excitons confined in the QD.

CuCl QD's were grown by heat treatment of a NaCl single crystal doped with 1 mol % of CuCl.⁹ The sample with average effective radius $a^* = 4$ nm defined in Ref. 10 was used for the present measurement. During the measurement, the sample was directly immersed in liquid nitrogen. The nonlinear optical response of the sample was measured by the pump-probe technique. Both pump and probe pulses were generated from a Rhodamine-6G dye laser ($\lambda = 608$ nm) with a Sulforhodamine dye amplifier (repetition rate = 1

kHz). The energy of the amplified pulse was 30 μ J and the autocorrelation width was 500 fs. The pump pulse was generated by frequency doubling of the 608-nm beam and the white probe pulse was generated by focusing the 608-nm beam onto a water cell. The energy density of the pump pulse was about 1 mJ/cm² on the sample surface. This density was adequate to generate multiple excitons in a QD (the mean number of the excitons per QD was estimated to be ~ 2), but low enough to avoid crucial damage of the sample. The arrival-time difference of each wavelength component of the white probe beam was corrected by taking into account the group-velocity dispersion of the optical media along the beam path. The luminescence spectrum of the sample was measured with the use of the same pump beam described above. The temporal change of the luminescence intensity was recorded by a streak camera with a time resolution ~ 20 ps.

Figure 1 shows the exciton absorption spectra of the CuCl QD without (solid curve) and with pumping (dashed curve, delay time $t_d = 10$ ps). The luminescence spectrum (dotted curve) excited by the same pump beam is also presented in the figure. In addition to the exciton luminescence band (Ex), the excitonic molecule band (M) was observed indicating that multiple excitons were created in a QD. The absorption spectrum measured with pump pulses shows obvious blueshift and broadening in both the Z_3 and Z_{12} bands. Further-

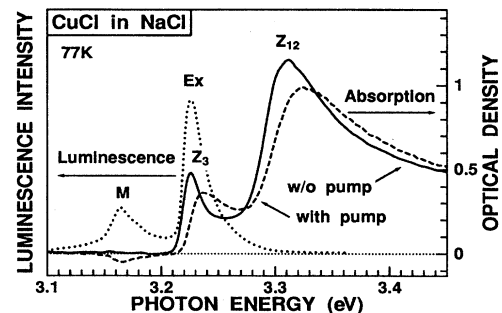


FIG. 1. Exciton absorption (solid and dashed curves) and luminescence (dotted curve) spectra of CuCl quantum dots ($a^* = 4$ nm) embedded in a NaCl crystal at 77 K. The solid and dashed curves represent the absorption without and with pumping (delay time $t_d = 10$ ps), respectively.

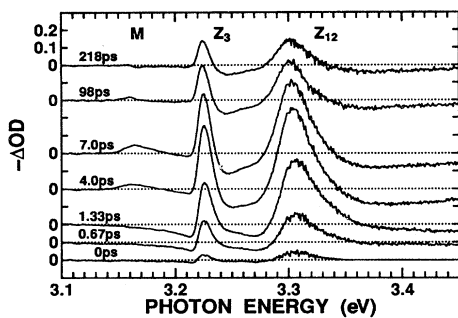


FIG. 2. Difference spectra of the exciton absorption of CuCl quantum dots at various delay times (t_d) between the pump and the probe. The reference of the absorption is taken at $t_d = -20$ ps.

more, negative optical density, i.e., optical gain due to excitonic molecules¹⁶ was observed in the energy region of the M band.¹⁴ Figure 2 shows the difference absorption spectra (ΔOD) at various delay times. The change around the Z_3 and Z_{12} bands grows rapidly within a few picoseconds, and lives for several hundred picoseconds. The optical gain at the M band grew after $t_d \sim 4$ ps, and lived for several tens of picoseconds. On the other hand, induced absorption, i.e., positive optical density, was observed in the M band in the early stage before $t_d \sim 4$ ps and after several tens of picoseconds.

Since the pump pulse causes shift and broadening of the absorption bands, it is important to analyze the temporal change in the spectral band shape.¹⁷ For this purpose, we apply moment analysis¹⁸ to the observed spectra around the Z_3 and Z_{12} bands. An advantage of this method is that we can numerically analyze the spectral band shape without assuming any specific functions. In the analysis, zeroth (M_0), first (M_1), and second (M_2) moments indicate the strength, the center-of-mass position, and the square of the band width, respectively. Thus, the change in the spectral band shape can be analyzed into three essential parameters: bleaching, shift, and broadening represented by the change of M_0 , M_1 , and $M_2^{1/2}$, respectively. The results of the moment analysis are shown in Fig. 3. The temporal change in the spectral band shape can be categorized into at least two components depending on the time scale. The first one is observed in the bleaching and the broadening; the bleaching and part of the broadening grow up and decay within $t_d \sim 5$ ps. This component is considered to be due to hot carriers initially generated in a QD by band-to-band excitation which could screen the Coulomb interaction^{1,2,19} and scatter the exciton. The decay time probably corresponds to the relaxation time from the hot electron-hole pair to an exciton. The second one is observed in the shift and the broadening; the shift and the longer decay component of the broadening remain for more than several hundreds of picoseconds. Thus, after several picoseconds, the change in the absorption bands mainly consist of the shift and a small amount of the broadening, but not bleaching. In addition, as discussed later, it is noteworthy that the shift of the Z_3 band grows with a rise time considerably slower than that of the Z_{12} band.

Figure 4(a) shows the temporal change of the ΔM_1 (shift) of the Z_3 and the Z_{12} bands on long time scales, and (b) shows the luminescence decay time of the excitons (Ex) and excitonic molecules (M). The decay profile of the shift is the

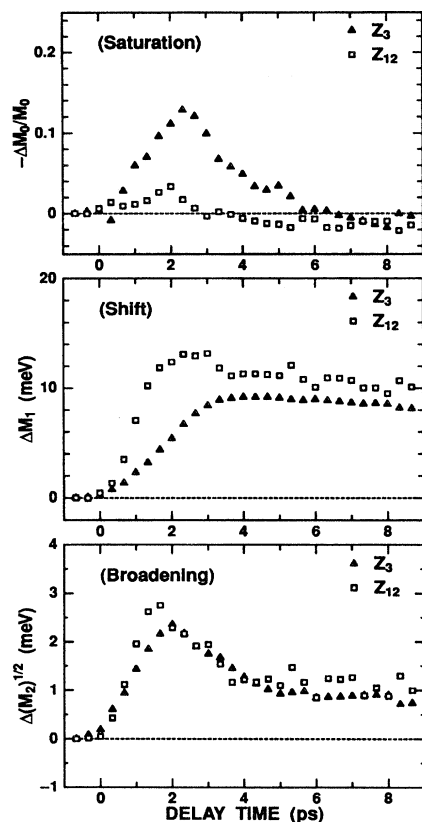


FIG. 3. Temporal change of the zeroth (M_0), first (M_1), and the square root of the second (M_2) moments of the exciton absorption spectra of CuCl quantum dots at various delay times. The reference is taken at $t_d = -20$ ps. The analysis was performed with finite but appropriately wide integration ranges around the Z_3 and Z_{12} exciton bands.

same for both of the bands and shows two components of decay time: $\tau = 60$ ps and $\tau = 380$ ps as shown by dotted curves in (a). These decay times correspond to the luminescence decay times of excitonic molecules (65 ps) and excitons (380 ps), respectively, as shown by broken curves in (b). This result clearly indicates that the shift is caused by the existence of an excitonic molecule and an exciton in a QD. Furthermore, the exciton luminescence grows with a rise time (65 ps) that is consistent with the decay time of the excitonic molecules, indicating the creation of single exciton through the radiative decay process of the excitonic molecule.²⁰

The excitation-induced blueshift of the excitonic absorption band of QD's has been observed by several authors.¹¹⁻¹³ However, its temporal change and a quantitative comparison with theoretical investigations have not been carried out so far. Our results indicate that the blueshift is caused by another exciton in a QD, as described above. This means that excitons confined in a QD are no longer ideal Bose particles because of strong interaction between individual electrons and holes in such a confined system, even in the exciton confinement regime.³⁻⁵ Although the energy shift in each QD should be essentially discrete, the observed shift varies continuously with time because of the considerable amount of inhomogeneous broadening due to size distribution of the

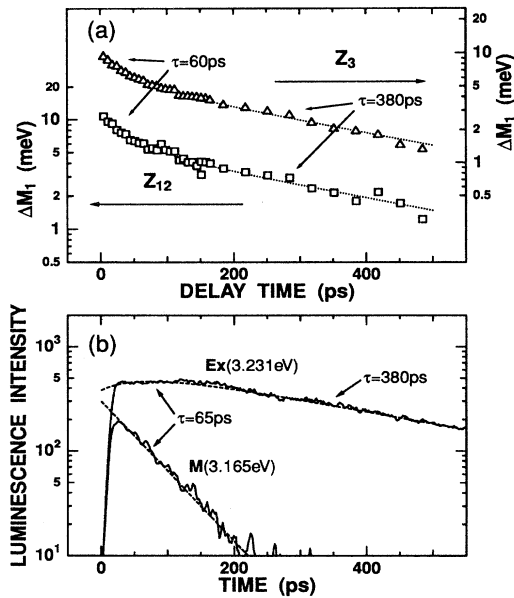


FIG. 4. (a) Temporal change of the first moments of the exciton absorption spectra of CuCl quantum dots for both the Z_3 and Z_{12} bands. (b) Temporal change of the luminescence decay both for the exciton (Ex) and excitonic molecule (M) bands.

QD's. However, by extrapolating the decay curve of the slowest ($\tau=380$ ps) component and taking account of the initial distribution of the number of excitons in a QD, one can estimate the shift due to an existing exciton in a QD to be 7 meV. In addition, the net effect due to an excitonic molecule is estimated to be twice that due to an exciton, indicating that the shift is essentially originated by the exciton-exciton interaction even if the excitonic molecule is created in a QD.

Based on the theory of density-dependent exciton-exciton interaction in bulk crystals, the interaction energy between two excitons in a QD is³

$$\Delta E = 6E_b \frac{m_e m_h}{(m_e + m_h)^2} \frac{a_b^2 f_0}{a^{*3}}, \quad (1)$$

where m_e and m_h are the effective masses of an electron and a hole, respectively, E_b and a_b the binding energy and the Bohr radius of an exciton, and f_0 ($=3.3a_b$ in CuCl) the scattering amplitude. By using the parameters of an exciton in bulk CuCl, one obtains $\Delta E=3.6$ meV for $a^*=4$ nm. On the other hand, based on the confined wave functions in a QD, the interaction energy between the two excitons is⁴

$$\Delta E = \frac{54.454}{1 + \delta_{n,n'}} E_b \frac{a_b^3}{a^{*3}} \int dX |\chi_n \chi_{n'}|^2, \quad (2)$$

where n and n' are the confinement quantum number, χ the confined wave function of the center-of-mass motion. For the case of $n=n'=1s$, which is the most dominant part for optical absorption, one obtains $\Delta E=19$ meV for $a^*=4$ nm. The experimental value (7 meV) is larger than the theoretical one for the bulk crystal [Eq. (1)], indicating the enhancement of the interaction between the confined excitons in a QD. However, since it is still smaller than that obtained by Eq.

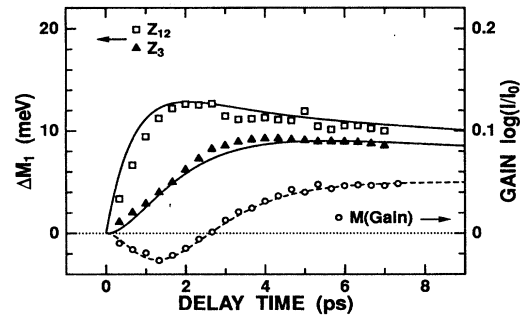


FIG. 5. Temporal change of the first moments of Z_3 and Z_{12} exciton bands and that of the optical gain at 3.165 eV. Solid and dotted curves are the calculated values based on the cascade relaxation model.

(2), more detailed investigations both in theory and experiment are necessary. Experiments including size dependence of the blueshift are now in progress.

The shift of the Z_3 band grew with a rate slower than that of the Z_{12} band. This result suggests that the cascade relaxation of an excited electron-hole pair to the Z_3 exciton state occurs through the Z_{12} state as an intermediate state. Furthermore, the optical gain due to excitonic molecules appeared after a longer delay time ($t_d \sim 4$ ps). This fact also suggests that an excitonic molecule in a QD is constructed just after the relaxation of two electron-hole pairs into the lowest Z_3 exciton state. In Fig. 5, we present the temporal change of the exciton band shift and that of the optical gain at the M band together with calculated curves based on the cascade relaxation model. In the calculation, the decay time from the excited electron-hole pair to the Z_{12} state and from the Z_{12} to the Z_3 state were both assumed to be 1 ps. Here, an empirical assumption was made that the shift of the Z_{12} band remains after the relaxation to the Z_3 state, reflecting the fact that both states are composed of a common electron in the same conduction band. The satisfactory agreement between the experiment and the calculation indicates that the cascade relaxation model adequately represents the exciton dynamics of the CuCl QD's. This cascade relaxation process is characteristic of the confined exciton system in a QD; in bulk crystal, however, such a process is hardly observed under the influence of the complex many-body interaction which exists at high density excitation conditions.

In conclusion, the excitonic optical nonlinearities of CuCl quantum dots mainly consisted of blueshifts of the Z_3 and Z_{12} exciton bands due to exciton-exciton interaction in a QD. The temporal change of the blueshift and the optical gain due to excitonic molecules was consistently interpreted in terms of the dynamics of confined excitons in a QD. These results clearly show that the excitonic optical nonlinearity in a CuCl QD is characterized by the number of the excitons per QD, which is classified into the exciton confinement regime.

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