



ELSEVIER

Journal of Luminescence 66&67 (1996) 401–405

JOURNAL OF
LUMINESCENCE

Infrared transient absorption of confined excitons in CuCl quantum dots

Yu Mimura, Keiichi Edamatsu, Tadashi Itoh*

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

Abstract

Infrared transient absorption of quantum-confined excitons from hydrogen-like 1S state to 2P state has been measured in CuCl quantum dots. The peak energy of the absorption band is dependent on the quantum-dot size and is much higher than the bulk value. The breakdown of the simple exciton confinement regime is discussed.

1. Introduction

In semiconductor quantum dots (QDs), exciton states show a blue shift in energy which depends on the QD size on account of the quantum confinement effect. It is well-known that the confinement effect on the lowest exciton state is classified into two extreme regimes [1]; “exciton confinement” for $a > a_{\text{ex}}$ (strong Coulombic interaction) and “electron-hole individual confinement” for $a \leq a_{\text{ex}}$ (weak Coulombic interaction) where a is the radius of QD and a_{ex} is the effective Bohr radius of the bulk exciton. In the former case where the translational motion of the exciton is confined, the energy blue shift is smaller than that in the latter case and their ratio is approximately given by a factor of μ/M . Here, μ and M are the exciton reduced mass and translational mass, respectively. The typical example for the former case is the confined exciton in nm-size CuCl QDs [2, 3], where $a_{\text{ex}} = 0.7$ nm and the exciton binding energy is 197 meV [4]. The lowest exciton state in CuCl QDs is approximately defined by the following two quantum numbers (1s,

1S); 1s due to the confinement inside a spherical quantum well potential and 1S due to the confinement inside a Coulomb potential, although they are no longer mutually independent good quantum numbers when both of the potentials are exactly taken into account in a QD. Here, a question arises for small CuCl QDs; what kind of classification is applicable to the exciton excited states, such as the 2S or 2P Coulombic excited state where the expectation value for the relative distance between the electron and the hole in the exciton is four times larger than a_{ex} ? No clear structure associated with the direct transition to the 2S exciton state in CuCl QDs could be observed in the absorption spectra or the excitation spectra of the exciton luminescence [3].

In this paper, infrared transient absorption of quantum-confined excitons generated with ns duration UV pulsed laser excitation is measured, for the first time, in nm-size CuCl QDs embedded in NaCl single crystalline matrices. The transient absorption band is decomposed into two components with different decay times. The faster decay component is assigned to the transition between the “Coulombic” 1S and 2P exciton states in a QD.

*Corresponding author.

The transition energy increases with the decrease of QD size and is much larger than the bulk value. The deviation of the 2P exciton state from the simple “exciton confinement” regime and the QD size dependence of the transition energy are discussed in comparison with the existing theory [5].

2. Experimental

CuCl QDs of two different sizes embedded in NaCl single crystalline matrices with the concentration of 1 mol% were prepared in the following way. First, a sample of CuCl QDs with an effective radius of 3.5 nm was prepared by the method mentioned in [3], and then annealed at 600 °C for 12 h in order to reduce the QD radius down to 1.3 nm. Here, the effective radius a^* of the QD was estimated from the magnitude of the blue shift, ΔE , of the Z_3 (1s, 1S) exciton, which is caused by the quantum-well confinement of the lowest 1S exciton in the “exciton confinement” regime and is given as follows [3]:

$$\Delta E = \frac{\hbar^2}{2M} \left(\frac{\pi}{a^*} \right)^2, \quad (1)$$

where M is $2.3m_0$ in CuCl QDs. Here, the effective radius a^* is somewhat smaller than the real QD radius a because of the exciton dead layer effect [3]. The samples were directly immersed in liquid nitrogen at 77 K. For the infrared transient absorption measurement, an XeF excimer laser (photon energy: 3.53 eV, pulse width: 19 ns, and maximum pump power: $I_0 = 33 \text{ mJ/cm}^2$) and an Xe flash lamp with MgF_2 window (pulse width: 8 μs) were used as a pump and a probe light, respectively. The pump photon energy is well above the lowest exciton energy even for 1.3 nm QD sample. The probe beam which passed through the excited region of the sample was analyzed by a prism monochromator in a wavelength region from visible to infrared up to 7 μm , detected by a CdHgTe photo-voltaic detector with a time response of 10 ns, and recorded by a digital sampling oscilloscope with 0.5 ns time resolution. Details of the experimental setup will be reported elsewhere [6].

3. Experimental results

Fig. 1 shows the luminescence spectra of CuCl QDs with $a^* = 3.5 \text{ nm}$ (solid line) and 1.3 nm (dotted line), respectively, after excimer laser excitation with the maximum pump power of I_0 . Broad bands indicated by E_x are the resonant luminescence of the quantum-confined (1s, 1S) exciton. The E_x peak energies are blue shifted from the bulk exciton energy (marked with a downward arrow) by $\Delta E = 13 \text{ meV}$ and 90 meV, from which the QD effective radii a^* are calculated with the use of Eq. (1) to be 3.5 and 1.3 nm, respectively. The broadening of the E_x band is inhomogeneous and is caused by the wide distribution of the QD size inside the samples [3]. Structures located on the lower-energy side and denoted by M are the biexciton luminescence associated with the confined-biexciton radiative decay into the (1s, 1S) exciton state [7, 8]. Existence of the M band with its intensity similar to that of the E_x band indicates that a considerable number of QDs contain one or two photo-generated excitons. This fact is consistent with a rough estimation of the number of excitons in a QD; the adopted pump power of $I_0 = 33 \text{ mJ/cm}^2$ gives the Poisson's distribution with one exciton per one QD on average.

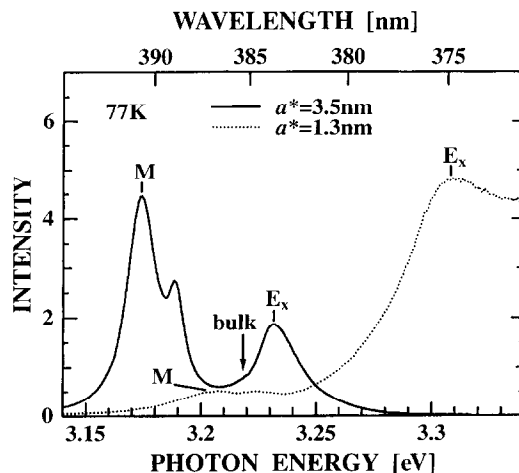


Fig. 1. Luminescence spectra of CuCl QDs under excimer laser excitation. Solid and dotted curves are for 3.5 nm QD and 1.3 nm QD samples, respectively. A downward arrow indicates the bulk 1S Z_3 exciton energy.

Transient absorption below the exciton energy down to 0.17 eV was measured under the same excimer laser excitation and strong transient absorption was found in the infrared region. At each wavelength, there exist two components with different decay times: a faster one, obtained by deconvolution, is a few ns which is the same order of magnitude as the decay time of the E_x luminescence, while the slower one is estimated to be a few hundred μ s, much longer than the probe pulse width of 8 μ s. In Fig. 2, the decomposed transient absorption spectra with faster (open circles) and slower (closed circles) decay times are compared among the two samples of different QD sizes under the pump power of $0.35I_0$. For the faster component, the peak energy, the bandwidth and the lower-energy edge of the absorption band are 0.28, 0.16 eV, and ~ 0.16 eV, respectively, for the 3.5 nm QD sample and 0.39, 0.25 and 0.2 eV for the 1.3 nm QD sample. The spectrum of the

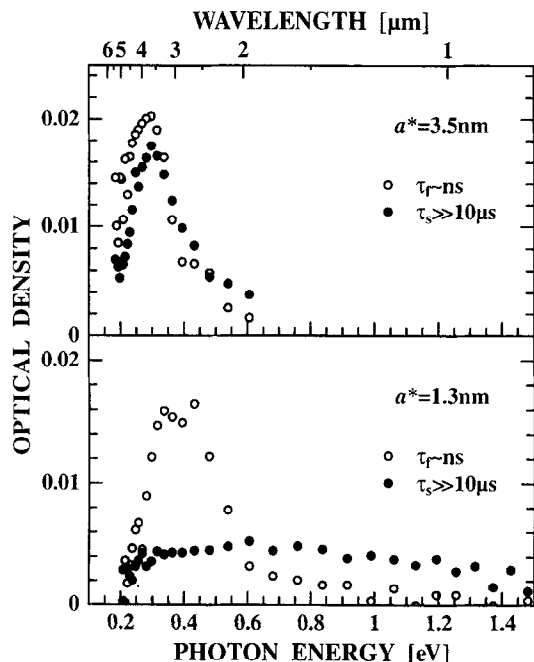


Fig. 2. Infrared transient absorption spectra for faster (open circles) and slower (closed circles) decay components. Upper and lower curves are for the 3.5 nm QD and 1.3 nm QD samples, respectively.

slower component for the 3.5 nm sample is not much different from the faster one, while for the 1.3 nm sample it is widely spread over the 0.2–1.5 eV region.

Excitation power dependencies were investigated both for the intensity of the E_x luminescence and the optical density of the transient absorption. Since the shape of the transient absorption spectra has no excitation power dependence between $0.1I_0$ to I_0 , the peak optical densities of the faster (open circles) and the slower (closed circles) components of the transient absorption are plotted in Fig. 3 as a function of the E_x luminescence intensity for different excitation powers. As shown by the broken line, the optical density for the faster component is proportional to the E_x luminescence intensity. Excitation energy dependence of the transient absorption was also examined by the use of a KrF laser (5.0 eV) instead of a XeF laser, but no significant difference could be observed although it was expected that the KrF laser could strongly excite Cu^+ monomers dissolved in NaCl matrix and also excite the NaCl matrix by two-photon absorption. These facts indicate that the transient absorption including both the faster and slower components are not directly related to the electronic states of the Cu^+ ions or NaCl matrix.

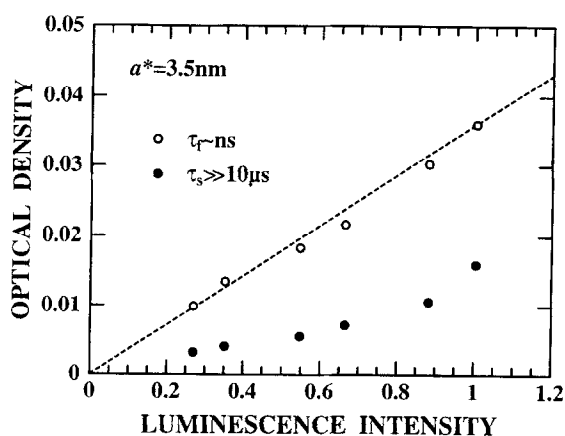


Fig. 3. Relation between the optical density of the transient absorption and the intensity of the exciton luminescence for different excitation powers. Faster and slower components of the absorption are shown by open and closed circles, respectively. A broken line indicates a linear dependence.

4. Discussion

The faster component of the transient absorption has a strong correlation with the confined exciton luminescence both in the time response and the excitation power dependence. Therefore, it is reasonable to consider that the absorption band is caused by the existence of the (1s, 1S) confined excitons. As a candidate for this transient absorption, one may first consider the optical transition from the lowest (1s, 1S) exciton state to the next (1p, 1S) excited state caused by the confinement of the translational motion of the 1S exciton inside the quantum well within the “exciton confinement” regime. However, in this case the transition energy should be nearly equal to ΔE , that is, less than 0.1 eV even for the 1.3 nm QD. Moreover, since this transition is not associated with the change of the electron–hole internal motion, the electric-dipole transition from the (1s, 1S) state to the (1p, 1S) state is forbidden if one does not take into account the mixing of the quantum-well confinement effect and the Coulombic confinement effect. Therefore, the most probable candidate for the transient absorption having a large oscillator strength is considered to be the transition from the (1s, 1S) state to the “Coulombic” 2P state (the 2S state is parity forbidden). This interpretation is supported by the fact that the lower-energy edge of the transient absorption is roughly equal to the bulk 1S–2P exciton transition energy of 0.17 eV [4]. Since the 2P exciton has the electron–hole relative distance larger than that of the 1S exciton, the “exciton confinement” regime does not hold for small QD size and, therefore, the state is only “2P-like”. This breakdown may be the reason why the transition energy increases so much with the decrease of the QD size. If the “electron–hole individual confinement” regime is fully applicable, the blue shift for the excited 2P exciton state is roughly estimated to be M/μ times larger than that in the case of the “exciton confinement” regime, and since $\mu = 0.39m_0$ and $M = 2.3m_0$ [3], the magnitude of the blueshift and the 1S–2P transition energy are estimated to be 90 meV and 0.25 eV for 3.5 nm QDs and 630 meV and 0.71 eV for 1.3 nm QDs, respectively.

More exactly, the Coulomb interaction should be appropriately considered. At present, no

Table 1

Comparison of the peak energy of the transient absorption (1S–2P transition energy) with the theoretically obtained 1S–2S transition energy [5] for samples with different sizes. The ratio a/a_{ex} is also given, where the exciton dead layer is taken to be about a_{ex}

Sample	Ratio a/a_{ex}	Present experiment 1S–2P transition (eV)	Theoretical calculation 1S–2S transition [5] (eV)
Bulk	∞	0.17 [4]	0.148
3.5 nm QD	6	0.28	0.17
1.3 nm QD	3	0.39	0.33

calculation has been given for the p-type exciton states in QDs. Instead, Kayanuma [5] has calculated the energy shift of several s-type (isotropically symmetric) excited states for arbitrary QD real radius a , including the “2S-like” exciton state which is extrapolated to the Coulombic 2S exciton state in the bulk crystal. Here, multiple anticrossing occurs among the “2S-like” Coulombic state and “ns-like” quantum-well confined states. The calculation depends on the hole-to-electron mass ratio σ and it is taken to be 5, being a little larger than 3.6 for CuCl QDs. According to his calculation, the effective QD radii of $a^* = 3.5$ and 1.3 nm defined by Eq. (1) roughly correspond to the ratios of $a/a_{\text{ex}} = 6$ and 3, that turn out to be about 0.17 and 0.33 eV for the 1S–2P transition energy as shown in Table 1, where the experimentally obtained values are also shown. Although the calculated transition energies are somewhat different from those obtained in the present experiment, it may be concluded that the excited states of the confined exciton in CuCl QDs is expressed not by the “exciton confinement” regime, but by the admixture of the Coulombic excited states and the quantum-well confined excited states, although the lowest (1s, 1S) exciton state is still classified into the “exciton confinement” regime. Some plausible reasons for the discrepancy between the experiment and the theory are as follows: (1) the “2P-like” state does not always show the strongest oscillator strength among the “nP-like” states because of the contraction of

the wavefunction for the electron–hole relative motion, (2) the QD size distribution in one sample widely broadens the transient absorption band and makes the peak energy position rather ambiguous [9], and (3) the calculation is not for p-like states but for s-like states, and even in the bulk crystal, the Coulombic P series has the binding energy smaller than that for the S series [4]. Further investigation on the experimental side is necessary with the use of size-selective pumping and probing, together with the help of the calculation of the transient absorption spectra for the 1S–nP transition in CuCl QDs.

Finally, the origin of the slower component of the transient absorption is briefly discussed. The absorption spectra for the faster and slower components are similar to each other in the 3.5 nm QD sample, implying an excitonic origin even for the slower component. While, in the 1.3 nm QD sample, the spectra are quite different. These facts may suggest that the absorption is associated with the formation of trapped electron–hole pairs, in which either of the constituent carriers is bound to the surface of the QDs, causing a long lifetime and a broadening of the transient absorption.

Acknowledgements

The authors are grateful to Prof. Y. Kayanuma for helpful discussions. This work was partially supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports and Culture of Japan.

References

- [1] A.L. Efros and A.L. Efros, *Sov. Phys. Semicond.* 16 (1982) 772.
- [2] A.I. Ekimov, A.L. Efros and A.A. Onushchenko, *Solid State Commun.* 56 (1985) 921.
- [3] T. Itoh, Y. Iwabuchi and M. Kataoka, *Phys. Stat. Sol. B* 145 (1988) 567; T. Itoh, Y. Iwabuchi and T. Kirihaara, *Phys. Stat. Sol. B* 146 (1988) 531.
- [4] K. Saito, M. Hasuo, T. Hatano and N. Nagasawa, *Solid State Commun.* 94 (1995) 33.
- [5] Y. Kayanuma, *Phys. Rev. B* 38 (1988) 9797.
- [6] K. Edamatsu, S. Hirota, Y. Mimura, T. Itoh and M. Hirai, in preparation.
- [7] T. Itoh, *Nonlinear Optics* 1 (1991) 61.
- [8] K. Edamatsu, S. Iwai, T. Itoh, S. Yano and T. Goto, *Phys. Rev. B* 51 (1995) 11 205.
- [9] For a $a^* = 3.3$ nm QD sample with a narrower size distribution, the peak energy of the transient absorption has been found to be 0.25 eV.