Size-dependent homogeneous linewidth of Z_3 exciton absorption spectra in CuCl microcrystals

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Size-dependent homogeneous linewidth of Z_3 exciton absorption spectra in CuCl microcrystals was measured at 2 K by the pump-and-probe spectroscopy. Observation of the hole burning gave us the homogeneous linewidth. The size-dependent part of the homogeneous linewidth is inversely proportional to the square of the radius of microcrystals. This dependence is explained by a simple model that a generated exciton dephases through the scattering at the irregular surface of microcrystals.

Recently much interest has been taken in the electronic and optical properties of semiconductor quantum dots, because of their unique properties and potential for device application.^{1,2} However, semiconductor quantum dots embedded in crystals or glasses have size inhomogeneity inherent in the preparation processes. The size inhomogeneity gives the scattering of the quantized energy and inhomogeneous broadening of the absorption spectra. Therefore, this obscures the noble properties of semiconductor quantum dots. The breakthrough of the study of the quantum dots is to make uniform-size quantum dots in a regular array. An alternative approach is to select dot by dot and examine the properties of the dot. The approach we took in this study is the latter, the size-selective laser spectroscopy of quantum dots.³⁻⁷

The samples we studied are CuCl microcrystals embedded in NaCl crystals where quantum confinement of excitons has been typically observed.¹ Quantum confined Z_3 excitons in CuCl microcrystals show blue shifts and the inhomogeneous size distribution causes broadening in the absorption spectra. We measured homogeneous linewidth of excitons in CuCl microcrystals by the hole-burning experiment. We performed the experiments in the pump-and-probe configuration and picked up the homogeneous linewidth from the inhomogeneously broadened spectrum by observing the burned hole. A very sharp (0.003 nm) dye laser was used to excite resonantly the Z_3 excitons in particular-size CuCl microcrystals. As a result of the size-selective excitation, CuCl quantum dots whose quantized energy of the Z_3 excitons is just equal to the laser energy are excited. Then we can observe a dip, that is, the burned hole in the inhomogeneously broadened Z_3 exciton absorption spectrum. We obtained the size dependence of the homogeneous linewidth Γ_h from the hole burning experiment for the first time. The homogeneous linewidth is an important parameter of excitons because it gives the phase relaxation rate of excitons in CuCl microcrystals. Nevertheless, the previous studies of the homogeneous linewidth are not free from ambiguities.^{4,8}

Two samples of CuCl microcrystals embedded in NaCl host crystals (Nos. 1 and 2) were used in this study. Absorption peaks of the Z_3 exciton in the No. 1 and No. 2 samples are 3.223 eV and 3.230 eV at 77 K, respectively. These samples were made from a mixture of NaCl powder

and CuCl powder. They were grown by the transverse Bridgman method. After preparing crystals from the melt, samples were annealed in order to control the size distribution of CuCl microcrystals. The molar fraction of CuCl was determined by the inductively coupled plasma optical emission spectroscopy. The volume molar fraction of CuCl is 0.16% for two samples. This low concentration of CuCl is essential to reduce the energy transfer between dots and to give the credible homogeneous linewidth, as shown in the following procedures. These samples have been mainly characterized by absorption spectra at 77 K. The Z_3 exciton lines of both the samples lie at an energetically higher spectral position compared with that of bulk crystals. This energy shift is due to the quantum size effect and expressed by $\hbar^2\pi^2/[2M(a + 0.5a_B)^2]$,⁹ where M is the translational mass of exciton, a is the radius of a microcrystal, and a_B is the Bohr radius of the Z_3 exciton. From the spectral position of the peak of Z_3 absorption, we estimated their mean radii. The mean radii of Nos. 1 and 2 are 6.1 and 4.1 nm, respectively. We also observed the broadening of the Z_3 absorption line, compared with bulk CuCl. This is explained by the inhomogeneous broadening due to the size distribution of the microcrystals.

The experiments were performed in a pump-and-probe configuration. An LD390 dye laser, whose wavelength was tunable from 380 to 390 nm, was used as a pump source. This laser was pumped by the excimer laser. The spectral linewidth of 0.003 nm was achieved in this dye laser system. The laser pulse duration was about 10 ns. As a probe source, we used the amplified spontaneous emission from a dye cell filled with BBQ dye solution. The excimer laser pulse also pumped the dye cell through a cylindrical lens. The probe pulse covered the broad spectrum ranging from 380 to 390 nm. The pulse duration was about 10 ns. The probe pulse through an optical delay impinged on the sample at the same time as the pump pulse hit the sample. There was no time delay between pump and probe pulses. In order to attenuate the probe pulse in front of the sample, we inserted a few neutral density filters. The probe beam was focused on the sample into a spot which lied inside a spot of the pump beam. The diameter of the pumped spot was several hundred micrometers. A polarizer was placed in front of the sample across the pump beam and another one behind the sample across the probe beam. Polariza-

FIG. 1. The absorption spectra of sample 2 obtained by the pump-and-probe experiment at 2 K. Burned holes (A)–(E) correspond to the pump photon energies of 3.2101, 3.2134, 3.2168, 3.2201 and 3.2235 eV, respectively. The excitation density is 146 kW/cm². The solid line shows the absorption spectrum without pump. Open circles show the base curve to extract the burned hole (A). The inset shows the fitting of the burned hole (A) by a Lorentzian. Solid circles show the hole. The fitting is shown by a solid line.

tions of two polarizers were crossed to each other so that most of the scattering of the pump beam was eliminated. The sample was directly immersed in superfluid helium (2 K) in a double Pyrex cryostat. The probe beam through the sample was analyzed by a double spectrometer and detected by a photomultiplier. The spectral resolution of our experiments was 0.01 nm. It was determined by the resolution of the spectrometer. The signal was amplified 10 times and averaged by means of a wide-band preamplifier and a Boxcar integrator.

Figure 1 shows the absorption spectra of sample 2 under the pump, obtained by the pump-and-probe experiment at 2 K. The photon energy of the pump pulse E_p was varied as 3.2101, 3.2134, 3.2168, 3.2201, or 3.2235 eV. The excitation density was 146 kW/cm². We observed the hole-burning around E_p .

The size of a microcrystal determines its quantized Z_3 exciton energy. Accordingly, we can selectively excite particular-size microcrystals by tuning E_p to their energy in the inhomogeneously broadened Z_3 absorption spectrum. Thus, each hole in Fig. 1 is burned out by the size-selective excitation. The pump energies in Fig. 1 correspond to the radii of 4.1, 3.7, 3.3, 3.1, and 2.9 nm, respectively. We also observed the hole-burning around E_p in sample 1 under the pump.

The line shape of the burned hole is well fitted by a Lorentzian as shown in the inset of Fig. 1. Therefore we need not take account of the effect of the energy transfer, in contrast with the previous fluorescence line narrowing measurement of a sample doped with 1% CuCl.⁴ This means that the CuCl concentration of 0.16% is low enough to reduce the energy transfer. In this case, the full width at half maximum (FWHM) of the burned hole 2Γ is equal to twice of the homogeneous linewidth Γ_h under the sufficiently weak excitation. Therefore, we should check the power broadening effect. We could not observe the power broadening in the power density range between 28 kW/cm² and 540 kW/cm². Therefore, FWHM of each

FIG. 2. The absorption spectra of sample 2 taken by the pump-and-probe experiment at various temperatures (from 4.2 to 65 K). The absorption peak is selectively excited in all cases. The excitation density is 490 kW/cm².

burned hole means twice of the homogeneous linewidth Γ_h .

We also measured the temperature dependence of $2\Gamma_h$. Figure 2 shows the absorption spectra of sample 2 taken by the pump-and-probe experiment at various temperatures. The Z_3 exciton absorption band shifts to the higher energy side with the increase in the temperature. Therefore, we tuned the pump photon energy E_p to the absorption peak and tracked the photon energy of certain-size microcrystals. In this experiment, the microcrystals of 4.1 nm in radius was excited at various temperatures under the excitation density of 490 kW/cm².

A broadening of the hole was observed with the increase in the temperature. Figure 3 shows the temperature dependence of the FWHM of burned holes $2\Gamma_h$. The broadening is caused by the exciton-phonon interaction. The phonon broadening of $2\Gamma_h$ is phenomenologically fitted by the form,

$$2\Gamma_h(T) = 2\Gamma_0 + CT^2.$$

The homogeneous linewidth at 0 K is $2\Gamma_0 = 0.59$ meV and

FIG. 3. The homogeneous linewidth of the Z_3 exciton absorption line in the microcrystal, whose radius is 4.1 nm, is plotted as a function of temperature. The solid line shows the result of fitting: $0.59 + 4.6 \times 10^{-4} \times T^2$ (meV).

FIG. 4. The homogeneous linewidth of the Z_3 exciton absorption line plotted as a function of the size of the CuCl microcrystal. The solid line shows the result of the fitting; $6.8 \times a(\text{nm})^{-2} + 0.14$ (meV).

a parameter C is 4.6×10^{-4} meV/K². The fitting is shown in Fig. 3 by the solid line.

We have already reported the broadening due to the exciton-optical phonon interaction.⁸ It is less than 0.03 meV below 70 K. Therefore, in this temperature range, the exciton-optical phonon interaction is negligible. Below 70-K exciton-acoustic phonon interaction is the dominant phonon broadening in the CuCl microcrystals. However, Fig. 3 shows that the temperature-dependent part of the broadening, phonon broadening, is at most smaller than $2\Gamma_0$ by an order of magnitude at 2 K. Therefore, the homogeneous broadening at 2 K should be explained by the exciton dephasing mechanism other than the exciton-phonon interaction.

Figure 4 shows $2\Gamma_h$ observed at 2 K as a function of the radius of microcrystals. The homogeneous linewidth Γ_h increases with the decrease in the microcrystal radius a . The relation between Γ_h and a is well expressed by the form

$$2\Gamma_h(a) = A \times a^B + 2\Gamma_{\text{bulk}},$$

where $2\Gamma_{\text{bulk}} = 0.14$ meV is the Z_3 exciton linewidth of bulk CuCl obtained by the two-photon absorption measurement below 10 K.¹⁰ The best fitting was obtained with parameters $A = 6.8$ meV nm² and $B = -2$ as shown in Fig. 4 by the solid line.

Here, we propose a simple model which explains this result, especially a^{-2} dependence. Theoretical study proved that the exciton quantization is a good picture when a is more than 4 times larger than the exciton Bohr radius a_B ($= 0.68$ nm).¹¹ Our study is just limited in this region where a is larger than 2.7 nm. Excitons are going and returning in a microcrystal and the exciton quantization takes place as a result of the interference between the going and returning exciton waves. In our model, the phase relaxation of Z_3 excitons takes place through the collisions at the irregular surface of microcrystals. The time in which the generated exciton moves and collides with the irregular surface of CuCl microcrystals determines the phase relaxation time T_2 . In this classical model, the velocity of an

exciton v in the lowest quantized state in a sphere whose radius is a is given by

$$v = \pi\hbar/Ma,$$

where M is the Z_3 -exciton translational mass of $2.3m_0$ (m_0 : electron mass). The phase relaxation time T_2 is given by,

$$T_2 = 2a/pv = 2Ma^2/\pi\hbar p,$$

where p is the dephasing probability of excitons at the surface. Therefore, the size dependence of the homogeneous linewidth is calculated as,

$$\hbar/T_2 = \pi\hbar^2 p / 2Ma^2 = 52p \times a(\text{nm})^{-2} \text{ (meV)}.$$

Thus, a^{-2} dependence of Γ_h is simply explained on this model. The calculated size dependence of the homogeneous linewidth agrees with that obtained by the experiments, if p is taken as 0.07. This means that an exciton in a CuCl microcrystal dephases at the surface irregularity during several periods of going and returning motion.

In summary, we obtained the size dependence of the homogeneous linewidth of Z_3 exciton absorption structures in CuCl microcrystals for the first time by the pump-and-probe experiment at 2 K. The size-dependent part of the homogeneous linewidth is inversely proportional to the square of the radius of the microcrystal. The size dependence is explained by a simple model that the phase relaxation of excitons takes place through the scattering at the irregular surface of the microcrystal.

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