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 $\Gamma_h$ 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.\(^8\)

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 $h^2 \pi^2 / [2M(a + 0.5a_b)^2]$,\(^9\) 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.

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 excitation density is 490 kW/cm². The absorption peak is selectively excited in all cases. The excitation density is 490 kW/cm².

FIG. 3. The homogeneous linewidth of the Z₃ 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 × 10⁻⁴ × T (K)² (meV).
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 $2.3 m_e$ (electron mass). The phase relaxation time $T_2$ is given by,

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

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

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

Thus, $a^{-2}$ dependence of $\Gamma_h$ 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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