Anomalous change of extinction spectra of CuCl microcrystals

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Optical transmission spectra of CuCl microcrystals embedded in NaCl crystals were studied around the Z_3 exciton resonance by varying the annealing time. With the increase in the annealing time, extinction spectra of the Z_3 exciton change anomalously from the absorption-type spectrum to the emission-type spectrum via the dispersion-type spectrum. The Mie theory [Ann. Phys. **25**, 377 (1908)] successfully explains the spectral change due to the growth of microcrystals. We report here for the first time an anomalous change of the exciton spectra due to the growth of semiconductor microcrystals.

Recently much interest has been taken in the linear and nonlinear optical properties of semiconductor microcrystals. Quantum confinement of electrons, holes, and excitons have been typically observed in CdS, CdSe, or CuCl microcrystals.[1] Especially, quantum confinement of excitons is well observed in CuCl microcrystals. Quantum confined excitons in CuCl microcrystals show blue shifts in the absorption spectra. In addition, the quantum confined excitons exhibit unique optical nonlinearities.[2] So far, the blue shift or the asymmetric line shape with a high-energy tail of the exciton absorption spectrum has been used to know the microcrystal size or size distribution.[3,4] However, the blue shift is detectable only for microcrystals whose radius is smaller than 10 nm. The all-optical means to estimate the arbitrary size of microcrystals is desirable. For the development of the all-optical means, the full understanding of the exciton absorption spectrum of microcrystals is important. It is also useful for the nonlinear optical study of microcrystals.

In this study, we studied the optical transmission spectra of annealed samples of CuCl microcrystals embedded in NaCl host crystals. We found the anomalous change of Z_3 exciton transmission spectra from the absorption-type spectrum to the emission-type spectrum via the dispersion-type spectrum with the increase of the annealing process time. The anomalous change was successfully explained by the Mie theory. Comparing the transmission spectra with the Mie calculation gives a unique optical method to estimate the microcrystal size. We demonstrated here that our all-optical method is useful to estimate the size of CuCl microcrystals.

Samples were grown from the molten NaCl doped with CuCl by the transverse Bridgman method. Many pieces of platelets were cleaved from a small block which was a part of a grown crystal rod. Their sizes were approximately $4 \times 4 \times 0.3$ mm^3. The doped CuCl concentration was determined to be 0.16 mol% by the inductively coupled plasma optical emission spectroscopy. Optical transmission spectrum of a platelet at 77 K is shown in Fig. 1(a). The vertical axis shows the extinction coefficient. It was simply calculated by $\ln(I_{in}/I_{out})/d$, where I_{in}, I_{out}, and d are the incident light intensity, the transmitted light intensity, and the sample thickness, respectively. The spectrum peak shows a blue shift of the Z_3 exciton by 3.6 meV from the bulk crystal. Asymmetric line shape with a high-energy tail

is due to the size distribution of the microcrystals. Platelets were annealed for 5, 40, 135, 320, or 625 min at 232 °C in vacuum. Transmission spectra of them at 77 K are shown in Figs. 1(b), 1(c), 1(d), 1(e), and 1(f). The Z_3 exciton structure in Fig. 1(b) is symmetric and is lower in height than that in Fig. 1(a). The Z_3 exciton structure in Figs. 1(c), 1(d), and 1(e) shows the dispersion-type structure. The structure in Fig. 1(f) shows the emission-type structure.

The similar spectral change is also observed around the $Z_{1,2}$ exciton resonance as is seen in Fig. 1. With the increase in annealing temperature, the same change takes place more sensitively depending on the annealing time. Reversely, with the decrease in annealing temperature, the
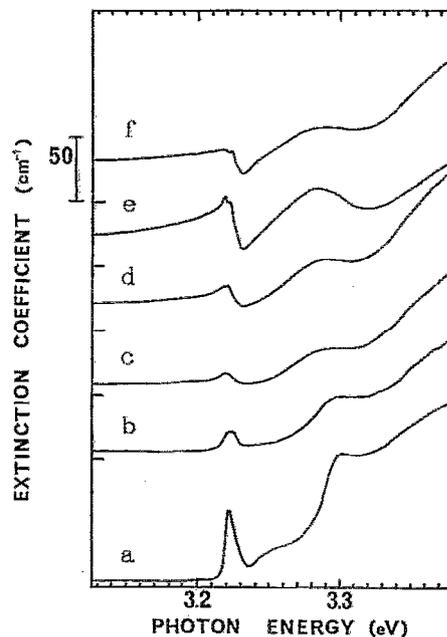
FIG. 1. Extinction spectra of CuCl microcrystals embedded in NaCl host crystals at 77 K. The spectrum a is the spectrum of a nonannealed sample. The peak energy shifts by 3.6 meV from the bulk position, which indicates that the radius of the microcrystal is 7 nm. The spectra b, c, d, e, and f are the spectra of samples annealed at 232 °C. The annealing time is 5 min for b, 40 min for c, 135 min for d, 320 min for e, and 625 min for f.

change becomes dull. We also measured the transmission spectra at 2 K to check the thermal broadening of the structure at 77 K. However, the structure changes little except an energy shift of 15 meV.

To our knowledge, this observation is the first report about the anomalous change of the exciton extinction structure in semiconductors. However, there are reports about the similar variation of the absorption bands in interstellar grains.[5,6] The phenomena have been interpreted by applying the Mie theory to the extinction spectra around the resonance line of the absorption bands. Therefore, we follow the similar analysis procedure.

We adopted the Lorentz oscillator model to describe the Z_3 exciton dispersion relation for simplicity. It is the one-oscillator model. The dielectric constant ϵ is described by the equation:

$$\epsilon = \epsilon_b [1 + E_l^2/(E_t^2 - E^2 - i\gamma E)] , \qquad (1)$$

where $\epsilon_b = 5.0$ is the background dielectric constant, $E_t = 3.2025$ eV is the transverse exciton energy, $E_l = 3.2080$ eV is the longitudinal exciton energy,[7] and $\gamma = 1.49$ meV is the damping constant. The damping constant γ is determined to describe the experimental ϵ_2 (imaginary part of dielectric constant) well.[8]

The mathematical procedures of the Mie calculation are as follows:[5] Suppose a microcrystal sphere is placed in the incident light flux. The electromagnetic fields at all the space points are expanded by the infinite series of Bessel functions. Here the Maxwell boundary condition is imposed on the fields at the boundary between a microcrystal sphere and the surrounding medium. Then, the scattering intensity and the transmission intensity of light are calculated at an imaginary sphere around the microcrystal and the intensities are integrated. In this way, we can calculate the scattering intensity, the extinction intensity and the absorption intensity which is equal to the extinction intensity minus the scattering intensity.

The calculation based on the Mie theory was numerically done by using the subroutine BHMIE.[5] Here, we assumed that CuCl microcrystals are spheres with a radius of a. The ϵ_1 (real part of dielectric constant) of NaCl host crystals is 2.457 around the Z_3 exciton resonance of CuCl and ϵ_2 of NaCl is assumed to be zero. Calculated spectra depending on the CuCl radius a divided by light wavelength λ are shown in Fig. 2. The light wavelength λ is fixed to be 387 nm. The vertical scale shows extinction, scattering, and absorption efficiencies by a CuCl microcrystal. The extinction efficiency is the sum of the scattering and absorption efficiencies. The efficiency is defined as the cross section divided by πa^2. The extinction cross section multiplied by the number density of microcrystals gives the extinction coefficient.

While the condition $a \ll \lambda$ holds, the electrostatic approximation is valid.[5] Then, the absorption efficiency increases in proportion to a with the increase in a. On the other hand, the scattering efficiency increases in proportion to a^4. Such scattering is referred to as Rayleigh scattering. The increase saturates as a/λ approaches to 0.1. When a/λ is 0.01, the line shape of the extinction efficiency spectrum
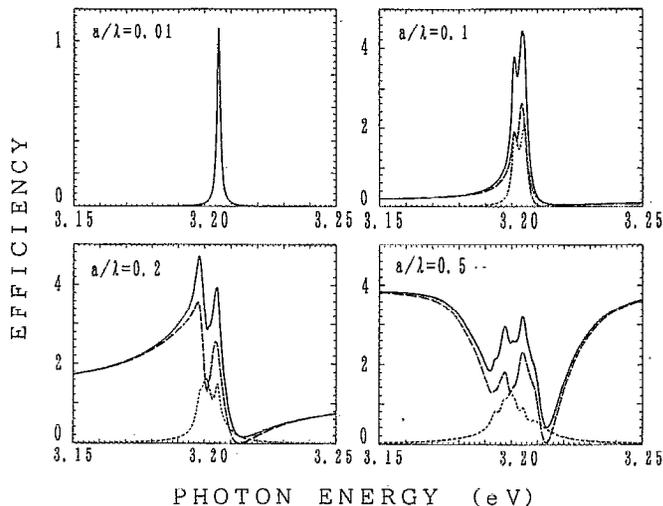
FIG. 2. Calculated extinction, scattering, and absorption efficiency spectra of a CuCl microcrystal embedded in an NaCl host crystal. The extinction, scattering, and absorption efficiency spectra are shown by solid, dashed, and dotted lines, respectively. The upper left, upper right, lower left, and lower right spectra correspond to conditions $a/\lambda = 0.01$, 0.1, 0.2, and 0.5, respectively.

is almost symmetric and most of the extinction comes from the absorption. The extinction spectrum shows a peak at the energy where $-\epsilon_1$ of CuCl is equal to twice ϵ_1 of NaCl. The peak is ascribed to the Fröhlich mode.[5] When a/λ is 0.1, the extinction spectrum becomes somewhat asymmetric and has a double-peak structure. Higher energy peak is ascribed to the Fröhlich mode and the lower energy peak to the low-frequency mode.[9] The scattering overwhelms the absorption. When a/λ is 0.2, the extinction spectrum is the dispersion type. The low-frequency mode overwhelms the Fröhlich mode. The scattering spectrum dominates the extinction spectrum. When a/λ is 0.5, the extinction spectrum is the emission type. The scattering dominates the extinction spectrum. The spectrum consists of multiple peaks which are ascribed to Fröhlich modes and low-frequency modes. The physical origin of the increase of modes is the increasing contribution of the higher-order electric-type and magnetic-type normal modes in the sphere with an increase in the radius.

In reference to the linear and nonlinear optical properties of semiconductor mycrocrystals, the local field effect in the electrostatic approximation has been considered for ultrasmall Rayleigh semiconductor microcrystals.[10,11] However, the treatment is not sufficient for CuCl microcrystals whose radius is larger than 0.1λ, because of the serious contribution of the scattering efficiency and the breakdown of the electrostatic approximation.

The calculated spectral change well explains the experimentally observed spectral change. With the increase in the annealing time, the size of CuCl microcrystals increases. As a result, the extinction spectra around the Z_3 exciton resonance change from the absorption type to the emission type via the dispersion type.

To compare the experimental extinction spectra with the calculated spectra, we took into account a size distri-

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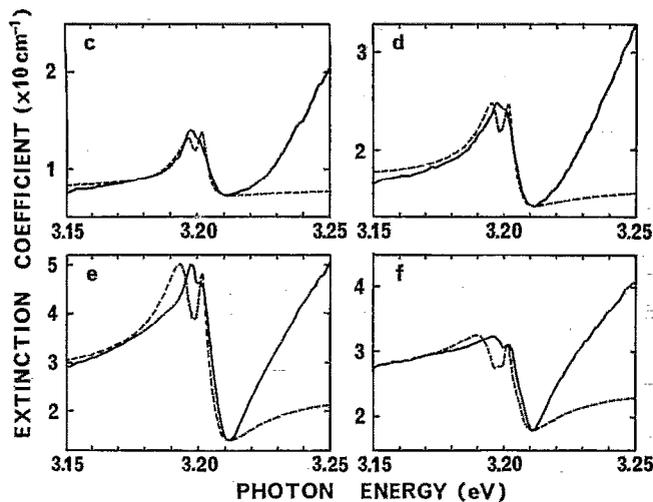
FIG. 3. Experimental (solid line) and calculated (dashed line) extinction spectra of CuCl microcrystals in NaCl host crystals. Figures c, d, e, and f correspond to Figs. 1(c), 1(d), 1(e), and 1(f), respectively. The horizontal energy scale is shifted by energy difference 15 meV between the Z_3 exciton resonance energies at 77 and 4.2 K. The vertical scales for the calculated spectra are chosen to be arbitrary to fit the experimental data well. The parameter a/λ values for the best fitting in c, d, e, and f are 0.14, 0.17, 0.20, and 0.25, respectively.

bution of the CuCl microcrystals. Larger microcrystals grow through the dissolution process of small microcrystals, the diffusion process and the recondensation process at larger microcrystals. In this case, the size distribution of CuCl microcrystals is considered to follow the Lifshitz–Slezov distribution.[4,12] The extinction spectrum is calculated by the integral

$$\int_0^{3/2} \pi a^2 P(a/\overline{a}) Q(E,a) d(a/\overline{a}) ,$$

where $\overline{a}$ is the average radius of microcrystals, $P(a/\overline{a})$ is the Lifshitz–Slezov distribution, and $Q(E,a)$ is the extinction efficiency spectrum of the microcrystal with a radius of a.

The experimental extinction spectra and fitted spectra are shown in Fig. 3. The experimental extinction spectra

and calculated spectra by the Mie theory agree fairly well with each other. Disagreement at the high-energy side of the Z_3 exciton resonance is ascribed to the neglected contribution to ϵ of the $Z_{1,2}$ excitons. We can estimate the approximate size of CuCl microcrystals by comparing the shape of the extinction spectra. The estimated radii of CuCl microcrystals for extinction spectra of Figs. 1(c), 1(d), 1(e), and 1(f) are 54, 66, 77, and 97 nm, respectively. As demonstrated here, the calculation based on the Mie theory is useful to estimate the radius of the CuCl microcrystals. This all-optical method is useful for CuCl Mie microcrystals whose radius a is in an order of $0.1\ \lambda$.

In summary, we observed the anomalous change of the extinction spectra of CuCl microcrystals embedded in NaCl host crystals with the increase of the annealing time. The Z_3 exciton structure changes from the absorption type to the emission type via the dispersion type. The Mie theory successfully explains the spectral change due to the microcrystal growth. Comparing the extinction spectra with the Mie calculation gives a unique all-optical method to estimate the microcrystal size. This report presents the first observation of the anomalous change of the exciton spectrum due to the growth of semiconductor microcrystals.

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