Lifetime of indirect excitons in AgBr quantum dots

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(Received 22 January 1992)

The lifetime of indirect excitons in AgBr quantum dots was studied at low temperature. Indirect-exciton luminescence shows a nonexponential decay. The unique nonexponential decay is well explained by a model that takes into account the discrete number of iodine impurities in a AgBr quantum dot. The obtained radiative lifetime of indirect excitons is 735 ± 50 μs at 2 K and is independent of the radius of microscrystals. The result clearly shows that the L-Γ mixing effect for holes does not work when the radius is larger than 3.5 nm.

I. INTRODUCTION

The optical properties of semiconductor quantum dots have been extensively studied because of their quantum size effect. So far, various phenomena in quantum dots of direct transition semiconductors, such as CdS, CdSe, and CuCl, have been clarified.[1] However, there is no report for quantum dots of indirect transition semiconductors except the previous two experimental reports for AgBr quantum dots.[2,3] AgBr is a well-known indirect-transition semiconductor and basic optical properties including impurity effects have been reviewed.[4,5] This allows us to examine the detailed optical properties of AgBr quantum dots. The preceding work on AgBr quantum dots has found quantum confinement of indirect excitons and isolation of impurities from quantum dots.[3] In this work, we focused our attention on the lifetime of the indirect excitons and found a unique nonexponential decay of indirect excitons. The experimental results are compared with a model which takes into account the discrete number of impurities in AgBr quantum dots.

II. EXPERIMENTAL PROCEDURES

AgBr quantum dots were prepared by the same method that is described in a previous paper.[3] Samples are AgBr microcrystals dispersed in porous gelatin. The mean radius of AgBr microcrystals is determined by the x-ray-diffraction linewidth and the experimentally derived relation between the mean radius and the linewidth, where the radius is measured by electron microscopy.

Samples are directly immersed in superfluid or normal fluid helium below 4.2 K. Above 4.2 K, natural temperature rise is used for the temperature dependence measurement. A photoexcitation source is a nitrogen laser (337.1 nm) or high-pressure mercury lamp. The measurement system is composed of a monochromator, a photomultiplier (Hamamatsu R1477), a boxcar integrator, a lock-in amplifier, and a digital storage oscilloscope (Iwatsu OS-6411; 40 MHz). For the time-resolved measurement, the temporal change of luminescence is taken by the photomultiplier and the digital storage oscilloscope. The temporal resolution is limited by the impedance mismatch between the photomultiplier and the oscilloscope and is experimentally determined to be 3.4 μs.

Excitation density is 160 W/cm^2. At this excitation density, we found that the luminescence exactly coincides with that taken by a high-pressure mercury lamp. We also found the temporal change does not depend on the excitation density between 25 W/cm^2 and 1.6 kW/cm^2.

III. EXPERIMENTAL RESULTS AND DISCUSSIONS

The photoluminescence spectrum of nominally pure AgBr bulk crystals at low temperature is well known.[4-6] It consists of two kinds of luminescence bands near absorption edge. One is phonon-assisted indirect-exciton luminescence peaks observed between 2.65 and 2.68 eV. They are classified into two groups, free-exciton peaks and shallow-bound exciton peaks. The second is a strong luminescence band observed at 2.5 eV which is ascribed to the bound exciton at a residual iodine impurity. The 2.5-eV luminescence band is much stronger than the indirect-exciton luminescence observed between 2.65 and 2.68 eV.

In the same manner as AgBr bulk crystals, AgBr microcrystals show two luminescence bands as shown in Fig. 1. The higher-energy band observed at 2.7 eV is ascribed to the indirect-exciton luminescence. The lower-energy band observed at 2.5 eV is ascribed to the bound exciton luminescence at iodine impurities. In contrast to AgBr bulk crystals, the indirect-exciton luminescence is strong compared with the bound exciton luminescence at iodine impurities. The ratio of the indirect-exciton luminescence to the bound exciton luminescence at iodine impurities increases more and more with the decrease in the radius of AgBr microcrystals. Another prominent feature observed in Fig. 1 is the blueshift of the indirect-exciton luminescence. The energy shift of the indirect-exciton luminescence is plotted in Fig. 2. Transverse-optical-phonon-assisted free-exciton luminescence in a bulk AgBr crystal is observed at 2.675 eV.[4-6] The blueshift is explained by the exciton quantization effect. The blueshift is well fitted by Kayanuma's calculation[7] with

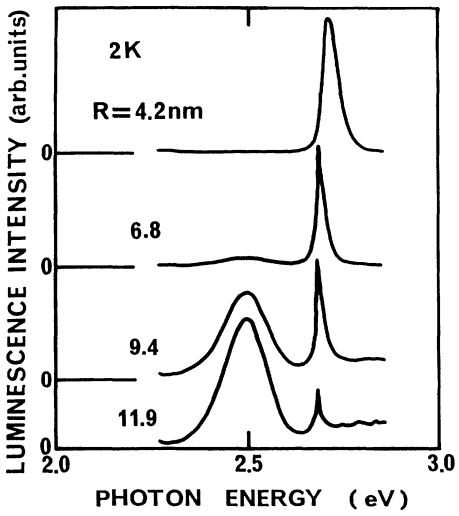

FIG. 1. Photoluminescence spectra of AgBr microcrystals at 2 K. The average radius R of microcrystals is 11.9, 9.4, 6.8, and 4.2 nm. The luminescence spectra are normalized by their respective peak intensities. The 2.7-eV band is indirect-exciton luminescence and the 2.5-eV band is bound exciton luminescence at iodine impurities.

parameters Ry=22 meV,[4] $a_B=2.5$ nm, $m_e=0.288m_0$, and $m_h=1.02m_0$,[8-10] where Ry is the Rydberg energy of the exciton, a_B the Bohr radius, m_e the electron band mass, m_h the hole band mass, and m_0 the electron mass, respectively. Another prominent feature observed in Fig. 1 are broad luminescence spectra, which are due to the size distribution of microcrystals. Because spectra are broad compared with the energy separation between the free exciton and the shallow-bound exciton, we think the free exciton and the shallow-bound exciton are not distinguishable from each other.

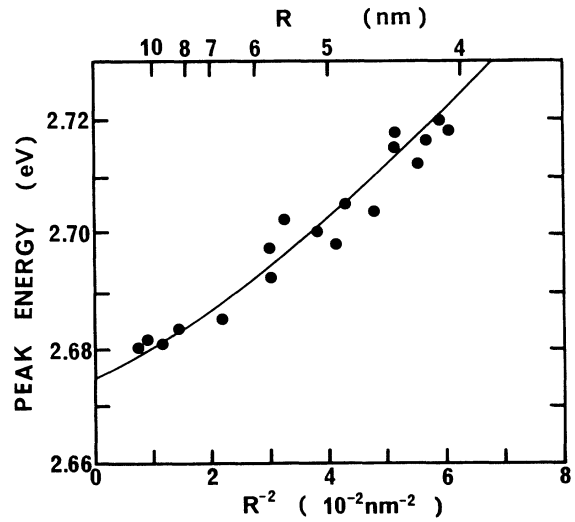

FIG. 2. Peak shift of the indirect-exciton luminescence plotted by solid circles as a function of radius of microcrystals. A solid line shows the fitted result.

Temporal change of indirect-exciton luminescence is shown in Fig. 3. Luminescence intensity is plotted on a semilogarithmic scale. Each curve corresponds to luminescence temporal decay at 2.748, 2.712, 2.700, and 2.689 eV, respectively. These energies correspond to radius of microcrystals of 3.5, 4.5, 5.2, and 6.6 nm, respectively. Luminescence shows nonexponential decays at initial time scale. However, the luminescence decay at the later time scale ranging from 200 μs to 1 ms is well explained by the single exponential decay. We note that the initial decay component increases with the increase in the radius.

We propose the following model to account for the temporal change of the indirect-exciton luminescence. AgBr quantum dots consist of 10^3-10^5 pairs of silver and bromine. The number of iodines in a AgBr quantum dot should be integer and should be 0, 1, 2, 3, or . . . . Usually, ultrahigh-purity AgBr crystals contain iodine impurities whose concentration is on the order of 1 ppm. Therefore a considerable amount of AgBr quantum dots is free from iodine. We assume the Poisson distribution for the number of iodine and other exciton killer impurity distribution for AgBr quantum dots.[3] Therefore the impurity number distribution $p(i)$ is expressed by $p(i)=(\lambda^i/i!)e^{-\lambda}$, where i is the impurity number in AgBr quantum dots, and λ is the expected value of the impurity number. In addition, we simply assume as follows. If a AgBr quantum dot has i impurities, the impurity capture rate of indirect exciton $1/\tau(i)$ is equal to i times of $1/\tau(1)$.[3]

On the basis of the above-mentioned assumptions, the temporal change of the indirect-exciton luminescence $L(t)$ is written by

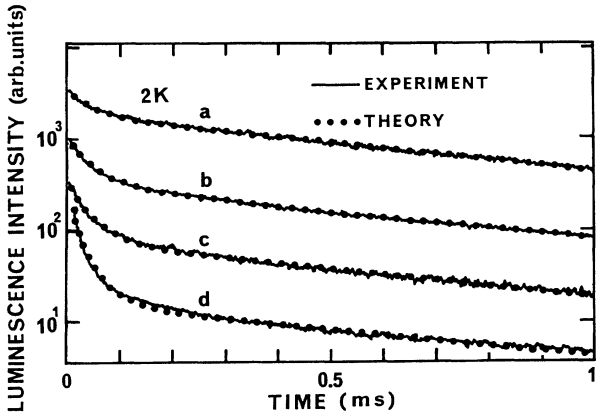

FIG. 3. Temporal change of indirect-exciton luminescence at 2 K. The experimental data a, b, c, and d shown by solid lines are those of microcrystals whose radius is 3.5, 4.5, 5.2, and 6.6 nm, respectively. The calculated results based on Eq. (1) in the text are shown by solid circles. Fitting parameters for curve a are $\tau(0)=719$ μs, $\tau(1)=68$ μs, and $\lambda=0.65$; those for curve b are $\tau(0)=725$ μs, $\tau(1)=54$ μs, and $\lambda=1.15$; those for curve c are $\tau(0)=749$ μs, $\tau(1)=54$ μs, and $\lambda=1.6$; and those for curve d are $\tau(0)=769$ μs, $\tau(1)=46$ μs, and $\lambda=2.7$.

$$L(t)=\sum_{i=0}^{\infty} p(i)e^{-t/\tau(i)}$$

$$=\sum_{i=0}^{\infty}(\lambda^i/i!)e^{-\lambda}e^{-t/\tau(i)}$$

$$=e^{-\lambda}\left[e^{-t/\tau(0)}+\sum_{i=1}^{\infty}(\lambda^i/i!)e^{it/\tau(1)}\right]$$

$$=e^{-\lambda}\{e^{-t/\tau(0)}+e^{\lambda\exp[-t/\tau(1)]}-1\}\ . \qquad (1)$$

In this way, the temporal change of indirect exciton is described by three parameters, $\tau(0)$, $\tau(1)$, and λ. Here, $\tau(0)$ means radiative lifetime of indirect excitons, $\tau(1)$ capture time of indirect exciton by an impurity ion in a AgBr quantum dot, and λ the expected value of the impurity number in a AgBr quantum dot.

The experimental temporal decay of the indirect-exciton luminescence is well expressed by a single exponential decay at the later time stage ranging from 200 μs to 1 ms. Therefore $\tau(0)$ is determined without uncertainty. Fitting the experimental data by Eq. (1), we can derive $\tau(1)$ and λ. The agreement between experimental data and the fitted values is perfect, which suggests the proposed model describes the physical processes of indirect excitons in AgBr quantum dots well. The obtained values of $\tau(0)$, $\tau(1)$, and λ are shown as a function of radius R of microcrystals in Fig. 4. The result clearly shows that $\tau(0)$ and $\tau(1)$ are independent of the radius R, but that λ increases with the increase of R. The value of $\tau(0)$ is about 735±50 μs. The value λ is proportional to $R^{2.1}$. The observation suggests that the impurity number is proportional to the surface area rather than the volume of microcrystals. This implies that the surface defects of microcrystals also work as exciton killer impurities.

So far, lifetime of indirect excitons in bulk AgBr crystals has been studied by several groups. It ranges from 10 ns to 100 ns and depends on impurity concentration, stress, and temperature.[8,11] The lifetime of 735±50 μs we obtained is much longer than values reported previously.

Figure 3 shows that $\tau(0)$ is independent of the radius R of the microcrystals. If the L-Γ mixing takes place in the Brillouin zone as claimed in a previous paper,[3] $\tau(0)$ should decrease with the decrease of the radius. Therefore the experimental data clearly deny the possibility of the L-Γ mixing. Here, we briefly discuss the L-Γ mixing effect in AgBr quantum dots. The wave-vector uncertainty Δk is almost equal to $1/R$, which is deduced from the uncertainty principle. Because the L point and the Γ point are separated from each other by $\sqrt{3}\pi/a$, L-Γ mixing takes place seriously only when Δk reaches $\sqrt{3}\pi/a$, where a is the lattice constant. The radius of the AgBr quantum dots we studied ranges from 3.5 to 13 nm, which is much larger than the lattice constant of $a=0.58$ nm. Therefore the mixing does not work in our case.

The hole mass at the L point m_h is $1.02m_0$.[8-10] The quantum confinement energy of holes at the L point in AgBr quantum dots is $\pi^2\hbar^2/(2m_hR^2)$ which is 30 meV at $R=3.5$ nm. The quantum confinement energy of holes is much smaller than the energy separation between the L point and the Γ point which is equal to 1.7 eV.[4] Therefore resonant L-Γ mixing hardly takes place.[12] Two kinds of the above-mentioned consideration support that the L-Γ mixing for holes does not work in our case.[13]

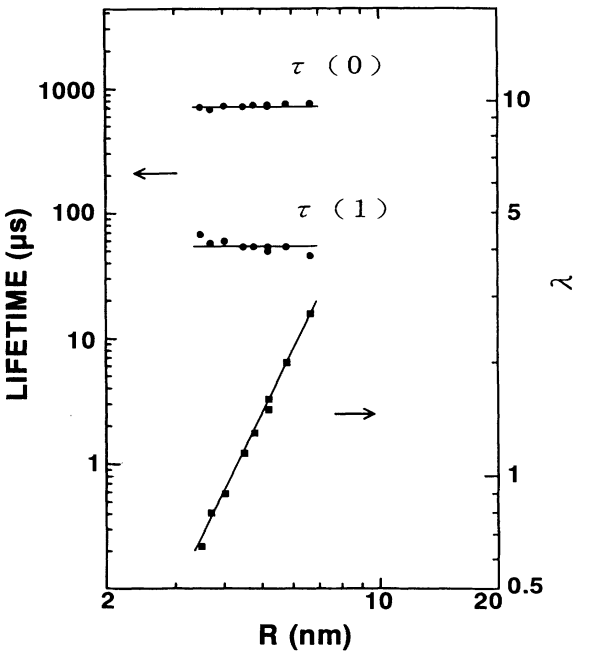

FIG. 4. The obtained parameters $\tau(0)$, $\tau(1)$, and λ as a function of the radius of microcrystals R.

The parameters $\tau(0)$, $\tau(1)$, and λ show weak temperature dependence below 20 K. This weak temperature dependence suggests the coexistence of the free indirect-exciton luminescence and the shallow-bound indirect-exciton luminescence which are observed in nominally pure AgBr bulk crystals. With the decrease of temperature, the shallow-bound indirect exciton becomes more stable. As a result, parameters show weak temperature dependence. With the decrease of temperature, $\tau(0)$ increases gradually. Above 20 K, the indirect-exciton luminescence is quenched, which indicates the increase of the nonradiative decay processes.

IV. CONCLUSIONS

Temporal change of indirect excitons in AgBr quantum dots is studied. Indirect-exciton luminescence shows a unique nonexponential decay which is composed of the initial fast nonexponential decay and the slow exponential decay. The experimental decay curves are well reproduced by a model which takes account of the discrete number of iodine impurities in a AgBr quantum dot. On the model, the slow exponential decay time constant is interpreted as the radiative lifetime of indirect excitons. It is 735±50 μs at 2 K and is independent of the radius of microcrystals. Radius-independent radiative lifetime informs us that the L-Γ mixing effect for holes does not work in our samples.

ACKNOWLEDGMENTS

The authors wish to thank Professor Emeritus H. Kanzaki, Professor Y. Kayanuma, and Dr. T. Takagahara for valuable discussions. They also wish to thank Dr. F. Sakuma at National Research Laboratory of Metrology for the kind loan of a standard lamp. A part of this work is supported by IKETANI Science and Technology Foundation and a Grant for International Joint Research Project from the NEDO, Japan.

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