Size effects on the temporal dynamics of edge emission in CdSe microcrystals embedded in a germanate glass matrix

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Picosecond time-resolved spectra of edge emissions in CdSe microcrystals with various sizes grown in a germanate glassy matrix are measured at 80 K. The temporal behavior of the edge emission exhibits multiexponential decay depending on the size of the crystal. The deconvolution analysis results in three decay components (F, S_1, S_2) that have different characters. The size dependence found in the decay time of the component S_1 agrees with a calculated dependence for the radiative lifetime of squeezed excitons. The component F with a decay time of about 20 ps originates from interactions of free carriers with trapped carriers.

INTRODUCTION

The physical properties of semiconductor microcrystals, whose dimensions range from a few nanometers to several tens of nanometers, are expected to differ widely from those of corresponding bulk crystals. Such small crystallites are called quasi-zero-dimensional mesoscopic systems in the sense that they show properties halfway between bulk (macroscopic) substances and molecularlike (microscopic) substances. The excitonic behavior of carriers generated in mesoscopic crystals is modified by the emphasized effect of the crystal boundary. Such quantum-confinement effects for the electron-hole pair are of much current interest and have been studied theoretically[1-9] and experimentally[10-20] by many authors. In particular, it has been found recently that semiconductor microcrystals embedded in a transparent matrix show large optical nonlinearity with a fast response time.[21-24] Although the materials which show such nonlinearities are candidates for potential applications, their fundamental properties (carrier dynamics, effects of surface and impurity states, etc.) are largely unknown. Investigation on the dynamics of photoexcited carriers in semiconductor microcrystals is necessary for further progress.

In this paper we report on the temporal dynamics of the edge emission of CdSe microcrystals with a germanate glassy matrix at low temperature, ~ 80 K. Bulk CdSe shows typical excitonic properties of Wannear type. The effective Bohr radius, $a_B^* = 4.5$ nm, is fairly large and, therefore, it is suitable for the observation of the effect of strong confinement on the exciton. The average crystal size of CdSe, d, was varied from larger to smaller size relative to $2a_B^*$. Since we want to reduce the effect of impurities which are transferred from the matrix to microcrystals, the matrix material was made with a composition as simple as possible. In these samples, the effect of the crystal size on the edge-emission decay was studied systematically. The size dependence of the decay behav-

ior is discussed based on the effect of spatial correlation between the electron and the hole through the Coulomb interaction and on the influence of trapped carriers. The interlevel separation of excited states is also considered significant.

EXPERIMENTAL

CdSe microcrystals in a glassy matrix were prepared through two processes. The first process was the synthesis of base glasses which contains Cd and Se ions as a supersaturated solid solution. The glassy matrix was composed of GeO_2 and Na_2O in a molar ratio of 92:8. Cd and Se elements of 0.3 mol % were mixed to the oxide materials described above. Then they were sealed in a quartz ampoule after evacuation down to 10^{-4} Pa. The ampoule was heated gradually up to 1180 °C, and rocked for 6 h in order to obtain a homogeneous sample. Then the melt was quenched in air, and we obtain base glass. The second process was the thermal annealing of the base glass for the growth of CdSe microcrystals. The size of the microcrystals was controlled by varying the temperature (500 °C–550 °C) and the duration (30–180 min) of the annealing. The average sizes of the microcrystals contained in respective samples were about 3–16 nm in diameter. These values were estimated, for the samples of $d > 7$ nm, by observations with a transmission electron microscope, and, for the other samples, by applying Brus's theory[2] to the energetic position of the absorption peak which corresponds to the lowest exciting energy. The error in the estimation of d is considered to be less than 10%.

For the excitation of photoluminescence, we used the 514.5-nm line of a continuous-wave mode-locked Ar^+-ion laser (Spectra Physics) which has the pulse duration of ~ 50 ps and the repetition rate of 82 MHz. As the photon energy of the exciting light is sufficiently larger than the lowest exciting energies for all samples, all crystallites in a sample can be excited homogeneously.[16] The

average excitation power was about 6.0 mW/mm^2 except for the case of the measurements of the dependence on exciting intensity. After the photoluminescence signal was dispersed by a polychrometer (Jovin Yvon HR-320), its temporal response was detected by a synchroscan streak camera with a two-dimensional detector (Hamamatsu C1587). The time resolution of the detection system is less than 10 ps. The wavelength width taken for the single measurement was 90 nm centered at the peak position of the edge-emission spectrum in each sample. The permanent change of optical properties by laser irradiation, or the photodarkening effect,[23,24] was not detected under the conditions of our experiment.

RESULTS

Figure 1 shows steady-state photoluminescence spectra taken at 80 K for CdSe microcrystals of three different sizes. The photoluminescence spectra mainly consist of two peaks. The narrow emission band of higher energy in each spectrum originates from the direct recombination of electron-hole pairs (edge emission), and is our interest at present. Although the intensity of edge emission in the sample of $d = 5.4$ nm seems to be very weak, it is fairly intense in the picosecond time domain. The broad band of lower energy originates from the recombination through defect states which exist mostly on the surface of microcrystals (surface emission). The surface emission in the sample of $d = 9.8$ nm appears almost an energy region lower than 1.5 eV. The decay time of the surface emission ranges from the order of nanoseconds to the order of microseconds.[25] The above assignments are according to the interpretation by Warnock and Awschalom[10] and Roussignol et al.[23] with respect to the results for commercially available color filters.

Figure 2 shows temporal profiles of edge emissions at energy positions of the spectral peaks for four different sizes of microcrystals. The temporal profile of the exciting laser pulses is also shown by the dashed line. The de-
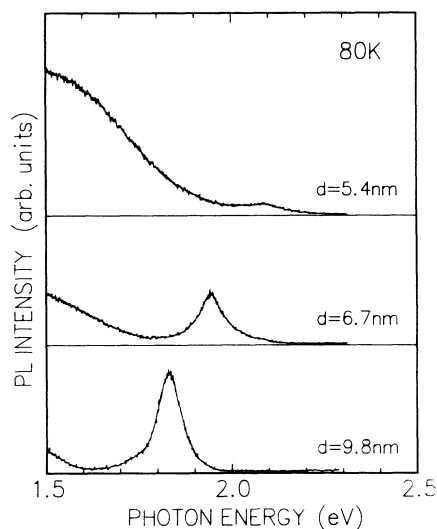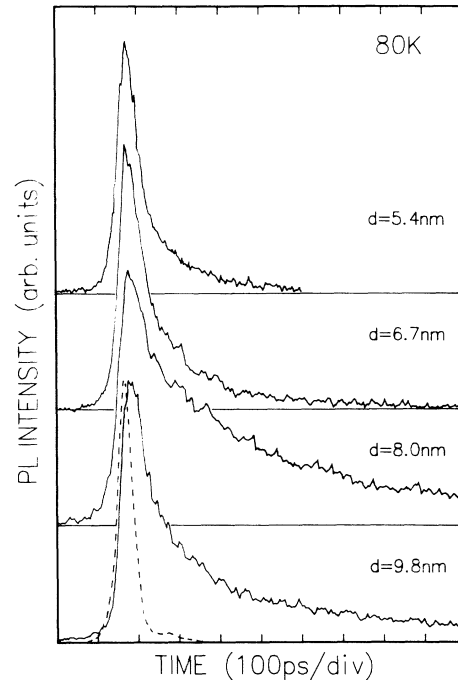

FIG. 2. Temporal profiles of edge emissions at peak positions of the spectra in samples of four different sizes (solid lines). The dashed line denotes a typical temporal profile of the exciting laser pulse.

cay behaviors did not show simple exponential ones and they are found to change depending on d. Figure 3 shows the edge-emission spectra for the sample of $d = 5.4$ nm at various time periods after excitation. Although the luminescence intensity decreases with elapsed time, no

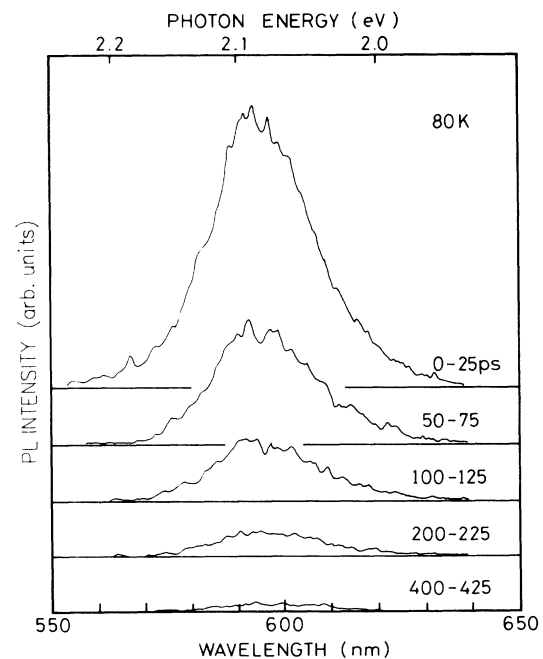
FIG. 3. Edge-emission spectra of the sample of $d = 5.4$ nm at various time periods after excitation. The time periods shown in the figure denote periods of averaging. These spectra are smoothed.

FIG. 1. Steady-state photoluminescence spectra of CdSe microcrystals in samples of three different sizes.

substantial change was observed in the spectral shapes. This behavior was sustained for all our samples. It implies that the components of different decay constants are attributed to the energetically same electronic transitions but different relaxation processes. The contribution of the surface emission to the time-integrated spectrum for a short time period (25 ps) is considered to be very small because of the very long decay constants relative to the observation period. If the tail of the surface emission contributed to the slow decay component, the peak structure should disappear as the fast component disappears.

The decay behaviors for all samples were analyzed using a least-squares fitting routine, asking for both the decay time and the time-integrated intensity of each component. We tried to fit the experimental data by a convolution of the temporal profile of exciting pulse and a sum of two exponentially decaying curves. This double-exponential fit could be performed successfully in the data of all samples except for that of $d = 8.0$ nm. For the data of $d = 8.0$ nm, a non-negligible misfit appeared. Therefore, the fitting was tried by triple exponential functions for this data. However, we note that the uniqueness of the parameters given by the triple-exponential fit was less reliable than that of the double-exponential fit.

These fittings, with the assumption of two or three decay constants, were made in order to clarify the size dependence of the decay behavior. Actually, the decay behaviors are not required to be expressed by only a few exponential components. The decay constants may have a continuous distribution which originates mainly from the distribution of size and shape of microcrystals. Nevertheless, the essential characteristics will not be lost in our simplifications.

In Fig. 4 the decay times of respective components are plotted as a function of d. We classified the decay constants into three groups and labeled the respective groups as components F, S_1, and S_2 (see Fig. 4). The component F is observed for $d < 8.0$ nm, and its decay time seems to be independent of d. The component S_1 is observed in all samples studied. The decay time of component S_1 in-

creases with decreasing d. The component S_2 is observed for $d > 8$ nm. In addition, it is an important result that the ratio of time-integrated intensity, I_F/I_S, steeply increases with a decrease of d as shown in Fig. 5. Here I_F and I_S are the intensities of the component F and S_1, respectively. The decay times of the major components in different size crystallites seem to agree reasonably with exciton lifetimes in microcrystals reported by Warnock and Awschalom.[12] Some differences would come from a difference in evaluating processes of the decay times.

We also investigated the dependence of the temporal behaviors of the edge emission on the exciting intensity for further information about the component F. In Fig. 6 the value of I_F/I_S is plotted as a function of excitation intensity for samples of $d < 6$ nm. I_F/I_S becomes larger with the increasing intensity of the excitation; that is, the component F is more pronounced by intense excitation. The temporal behavior under intense excitation agrees with the observation by Roussignol et al.[23] They have reported a very fast decay, unresolved even with 28-ps pulses. They have probably used considerably more intense pulses and could not resolve the decay due to instrumental limitation.

Our results suggest that the component F is not governed by the trapping process of excited carriers to defect states. If trapping of excited carriers to defect states causes such fast decay as the component F, the relative intensity of the component should be reduced when the exciting intensity becomes larger. The intense excitation would saturate the trap states due to their considerably longer lifetime of carriers and carrier trapping could not occur. Here we mention the work by Nuss, Zinth, and Kaiser.[13] They have measured the absorption recovery time of filter glasses by a pump-probe method and reported a contrary result to ours: the increase of the slow component with increasing intensity of pumping. Their result denotes the cooling-down process of hot distribution of carriers; it may be different from our result which corresponds to the relaxation process of quasi-thermalized carriers. They have also not clearly specified the sizes of microcrystals.
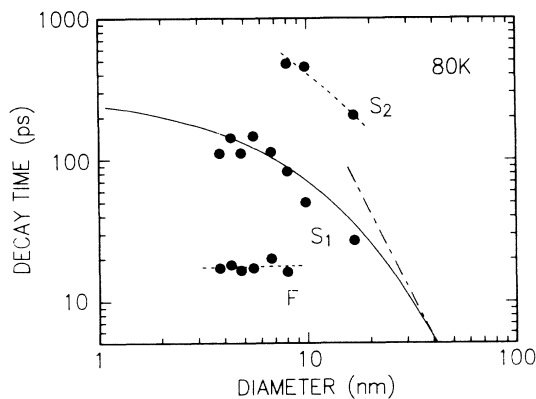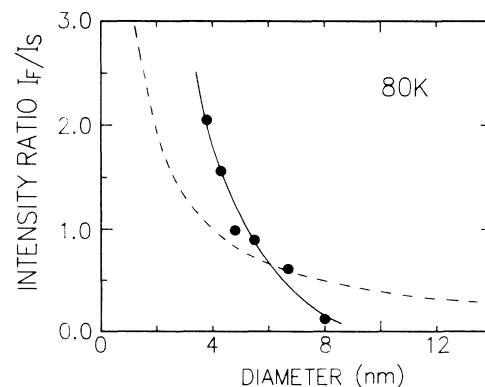

FIG. 4. Size dependences of decay constants obtained by our fitting (solid circles). The decay components of three different characters are labeled as shown in this figure. The solid line denotes the calculated dependence of the radiative lifetime of squeezed excitons. The dashed-dotted line denotes a d^{-3} dependence.

FIG. 5. Dependence of intensity ratio I_F/I_S on the crystal size (solid circles). The dashed line denotes the d^{-1} dependence of the surface-to-volume ratio of a crystal.
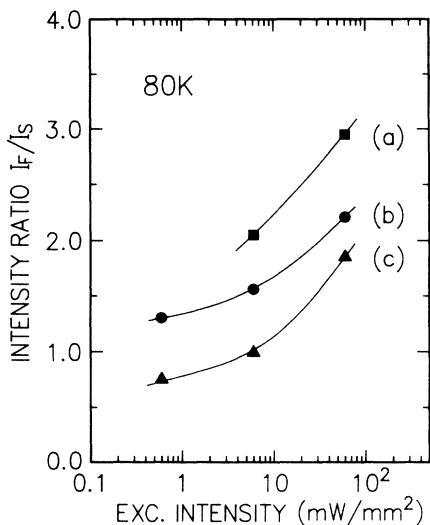
FIG. 6. Dependence of I_F/I_S on the exciting intensity in samples of (a) $d = 3.2$ nm, (b) $d = 4.3$ nm, and (c) $d = 4.8$ nm.

DISCUSSION

The comparable size of microcrystals to the spatial extension of the exciton in a bulk crystal brings about the strong modification of the excitonic states. The wave function of a generated electron-hole system is affected by the crystal boundary rather than the Coulomb interaction, so the kinetic energy often overcomes the electrostatic energy.[2,3] In this case, the picture that the electron and hole are individually confined without spatial correlations is a good approximation. It has explained the optical properties of semiconductor microcrystals of many kinds under static conditions, e.g., the size dependence of the threshold energy in the optical absorption, etc. Within the above approximation, Brus[2] estimated the oscillator strength per microcrystal with respect to the transition to the lowest excited state which is responsible to the radiative lifetime of the confined electron-hole pair. The result predicted that the oscillator strength is basically independent of the crystal size except for the weak variation which comes from the blueshift of the transition energy due to the quantum size effect. This may be true for the crystal of very small size relative to $2a_B^*$, but not for the crystal of the size around $2a_B^*$. The Coulomb interaction should be included more exactly in our case.

The variational calculations by Takagahara[6] and Kayanuma,[9] which take account of the spatial correlation between the electron and the hole through the Coulomb interaction, have supplied a more detailed dependence of the oscillator strength on the size of the crystal. There the spherical shape of crystals and infinite barrier height at the crystal surface were assumed and the variation of the transition frequency, depending on the size, was neglected. Their results appear as enhancement factors to the oscillator strength of the uncorrelated electron-hole pair as a function of the ratio of crystal radius to a_B^*. They are essentially identical to each other, though the expressions are different. The electron-hole pair with

spatial correlation can be regarded as a squeezed exciton in a microcrystal. On the other hand, the uncorrelated electron-hole pairs in microcrystals can correspond to free carriers in bulk crystal. The binding energy of the squeezed exciton is then defined by the energy difference, depending on the correlation existing or not.[6]

In Fig. 4 the calculated curve was shown by a solid line. Here we used the value of 250 ps for the radiative lifetime of the uncorrelated electron-hole pair in microcrystals. This value was determined by using the data of the edge-emission decay taken at room temperature. A typical decay behavior of the edge emission at room temperature is presented in Fig. 7. Those data show double-exponential decays with ~ 10- and 250-ps components, and are nearly independent of d. At room temperature, the spatial correlation between the electron and the hole should be lost because of the small binding energy which is the same order of magnitude as that of the bulk crystal.[6] Therefore, the decay constant of the slow component at room temperature can correspond to the lifetime of the uncorrelated electron-hole pair. The origin of the ~ 10-ps component is considered to be the same as that of the component F, and it will be discussed below.

The size dependence of the decay time for the component S_1 agrees with the calculated curve fairly well. This fact suggests that the component S_1 corresponds to the component due to the radiative decay of squeezed excitons. And it proves consistently that the slow component at room temperature is attributed to the lifetime of an uncorrelated electron-hole pair. It demonstrates the deviation in the realistic case from the ideal picture of the individual confinement of the electron and the hole.

The radiative lifetime which varies proportionally to the reciprocal of the crystal volume is predicted for sizes larger than those we studied.[8] We unfortunately could not confirm the prediction because we could not prepare the sample of $d > 16$ nm. However, if we could, it is questionable for CdSe whether such a dependence would be observed or not, because of the following reasons. Since the energy separation between the lowest excited state and higher excited states becomes so small (5 meV for CdSe of $d = 30$ nm) with increasing the size, the quasithermalized carriers are distributed in higher excited states at finite temperature. The radiative recombination from the lowest excited state would then become difficult to be observed.[8] When the energy separation be-
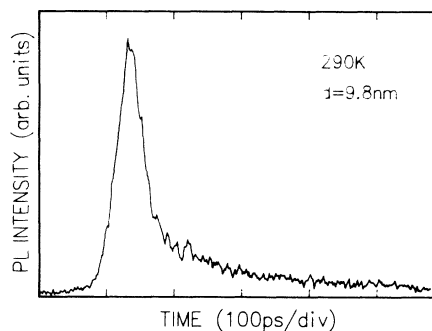

FIG. 7. Temporal behavior of edge emission at room temperature.

comes close to their homogeneous linewidth, the mixing of states would become possible. In fact, the behavior of the component S_2 supports the above considerations. The component S_2 increases the relative intensity with increasing d, and possibly masks the component S_1 in larger d than we studied. So we assign the component S_2 to the higher excited states close to the lowest excited states. However, we cannot explain at present the meaning of the decay time of the component S_2, or why the components S_1 and S_2 show a double-exponential decay.

The interpretation for the component F requires careful consideration of the relevant data. As seen in Fig. 5, the dependence of I_F/I_S on d shows an increase with decreasing d. Although the increase of component F suggests the relation to the increase of surface states, the dependence is much steeper than the d^{-1} dependence simply expected from the variation of the surface-to-volume ratio with d. It implies that the variation of the I_F/I_S cannot be explained only by the relative increase of surface states. On the other hand, I_F/I_S increases with increasing intensity of the excitation, but the dependence is rather weak.

The appearance of the component F is related to the presence of trapped carriers on surface states of microcrystals. The density of trapped carriers can be regarded as a stationary constant depending on the average power of the excitation, because the interval ~ 12 ns of exciting laser pulses is much shorter than the lifetime $\sim \mu$s of the trapped carriers. The density increases slowly with increasing intensity of excitation. As it is similar to the dependence of I_F/I_S on the exciting intensity, the origin of the component F is suggested to be based on the interaction of squeezed excitons with trapped carriers. The interaction of the confined electron-hole pair with trapped carriers has been recently introduced by Hilinski, Lucas, and Wang.[15] According to them, the photoexcited electron (hole) is localized to some extent by the trapped hole (electron), resulting in the reductions of the energy and the oscillator strength.

We assign the decay time ~ 20 ps of the component F to the capture time of squeezed excitons by trapped carriers. Under weak excitation, all excitons may not be captured because the trapped carriers which interact effectively with excitons would not exist in all microcrystals. Therefore, the component S_1, due to the radiative decay of squeezed excitons, is then observed with the component F. With increasing intensity of the excitation,

the number of trapped carriers increases and the probability of capturing increases. So, the component F becomes pronounced. The carriers bound to trapped carriers would decay with a long lifetime reflecting the reduced oscillator strength, or decay nonradiatively. In our preliminary study with respect to the surface emission, a weak emission with ~ 1-ns decay time was observed below the edge-emission energy only for the samples of $d < 6$ nm, separately from microsecond components.[25] As one of several possible cases, this nanosecond component may be due to the radiative recombination of such bound carriers.

The capturing process involves the breaking of the electron-hole correlation. So, the steep increase of I_F/I_S with decreasing size is partially due to the decrease of the electron-hole spatial correlation. As the character of the individual confinement becomes active with decreasing size, the capturing by trapped charges becomes more efficient because the process originally stands on the individual carrier of the electron or the hole. In other words, as the hydrogenic character of the electron-hole correlation appears with increasing size, the electron-hole pair becomes to behave as a single particle. Then the respective carriers become difficult to interact with trapped carriers individually. Therefore, the component F is reduced with increased d.

CONCLUSION

In conclusion, we have investigated the dynamical property of squeezed excitons in CdSe microcrystals by means of time-resolved spectroscopy of edge emission at low temperature. The rather complicated behavior of the edge emission decay has been studied by a systematic examination of the size dependence. We have demonstrated that, in CdSe microcrystals, the spatial correlation between the electron and hole due to the Coulomb interaction affects their lifetimes. Thermal effects are invoked as being responsible for the decay behaviors. The fastest decay component of about 20 ps has been attributed to the capturing process of free carriers by trapped carriers.

ACKNOWLEDGMENTS

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