Quantum-confined Stark effects in $CdS_{1-x}Se_x$ quantum dots

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Quantum-confined Stark effects (QCSE's) on exciton-decay dynamics in $CdS_{0.31}Se_{0.69}$ semiconductor quantum dots (QD's) embedded in a glass matrix have been studied by time-resolved photoluminescence emission spectroscopy under different electric fields up to 2.5×10^5 V/cm. Under both conditions, in the absence or in the presence of an applied electric field, the exciton luminescence decay in QD's is found to follow the stretched exponential function $I(t)=I_0\exp(-At^{\beta})$. The decay rate A and exponent β are found to vary linearly with the applied electric field, which can be accounted for by the field-induced reduction of the confined electron and hole wave-function overlap in QD's. The QCSE observed in the QD's is weaker than those observed in semiconductor quantum-well structures.

Semiconductor quantum dots (QD's) have attracted considerable attention because of their unique optical properties due to quantum confinements.[1-4] So far, the emphasis has been on carrier confinement, effects of surface on carrier recombination, and energy levels. Recently, electroabsorption has been observed in $CdS_{1-x}Se_x$ QD's and quantum-confined Stark effects (QCSE's)—effects of an applied electric field on confined carriers—have also been studied in QD's by electroabsorption experiments.[5,6] Previously, QCSE's have been studied in quantum-well (QW) structures, but have not been studied extensively in a truly confined system, namely in a quantum-dot system. In this paper, we report an experimental observation of QCSE's in $CdS_{1-x}Se_x$ QD's through time-resolved exciton photoluminescence measurements. A strong QCSE on the exciton dynamics in QD's has been observed. A field-induced linear reduction in the exciton decay rate has been observed up to an applied electric field of 2.5×10^5 V/cm. A calculation based on the perturbation theory has also been performed, which shows that the decay rate decrease is due to the field-enhanced spatial separation between electrons and holes of the confined excitons in the QD's.

The sample used for this work was a red color glass filter containing $CdS_{1-x}Se_x$ semiconductor QD's provided by Kopp Glass, Inc. The Se composition is about 0.69 as determined by the company, and 0.71 as determined by our photoluminescence measurement. The average size of the $CdS_{1-x}Se_x$ QD's was about 90 Å, as determined by transmission electron microscopy (TEM) measurement. The sample size was about 0.24 mm in thickness, with a 1×1-cm^2 surface area. For the application of an electric field, transparent conducting layers of indium-tin oxide (ITO) were deposited by the evaporation method on both sides of the sample.[7] The area of the ITO layers was a little bit smaller than the surface area of the sample, in order to prevent electric-field breakdown near the edges. The evaporation technique was then used again to deposit indium as electrical contacts. Gold wires were then soldered directly onto indium contacts. Figure 1 is the schematic diagram showing our QCSE experimental setup. The electric field was supplied by a dc power supply (0–20 kV). The maximum voltage applied to the sample was 6 kV, which corresponds to an electric field of 2.5×10^5 V/cm across the sample, and a field breakdown between the two electrodes through the glass matrix (not edges) was observed above this field value.

During experimental measurements, the sample was held inside a closed-cycle He refrigerator. Photoluminescence spectra were collected in a reflecting mode. An excitation laser pulse of about 7 ps at a repetition rate of 3.8 Mhz was provided by a cavity-dumped dye laser (Coherent 702-2CD) with rhodamine 6G dye solution, which was pumped by an yttrium-aluminum-garnet (YAG) laser (Coherent Antares 76) with a frequency doubler. The dye laser photon energy was set at 2.156 eV, with a spectral width of about 0.3 meV. The laser excitation intensity for the experiment was about 100 W/cm^2, corresponding to the low intensity region, so Auger recombination could be neglected.[8,9] A single photon-counting detection system was used to record the time-resolved photoluminescence spectra. The overall system resolution is about 0.1 meV in energy and about 0.1 ns in time with a deconvolution technique.

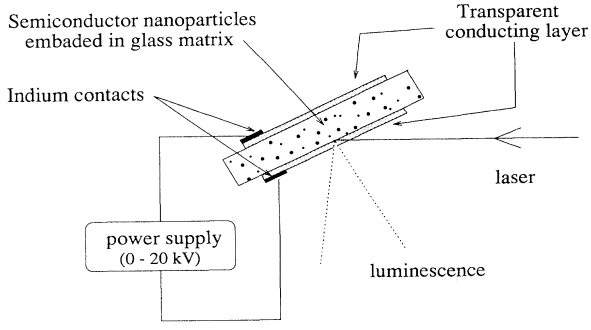

FIG. 1. The schematic diagram of experimental setup for the QCSE measurements.

Figure 2 shows exciton luminescence emission spectra of $CdS_{0.31}Se_{0.69}$ QD's obtained at two different temperatures $T=10$ (● ● ●) and 40 K (○ ○ ○). Both emission spectra show broad linewidths with a full width at half maximum (FWHM) of about 47 meV. The peak position shifts toward low energies as the temperature increases due to the energy-gap variation with temperature. The broad linewidth of the exciton luminescence in QD's has been attributed previously to the particle size distribution.[10] On the other hand, compositional fluctuations can also contribute to the linewidth broadening in alloy QD's.[11] In $CdS_{1-x}Se_x$ alloy QD's, with increasing size, the confinement energy decreases; however, the same emission energy can still be retained if the energy gap of the QD is subsequently increased by decreasing x. Thus luminescence at a fixed emission energy E is contributed from QD's with different sizes and different compositions. Previously, we have fitted time-integrated emission spectra by assuming both the size and composition distributions following the Gaussian distributions.[12] By using a value of r_0 (=90 Å) as determined by TEM measurement, the fitted value of x_0 was 0.71, which agreed reasonably well with the value determined by the company. The overall fitting of the emission spectra was also quite good except for the low-energy tail, which was most likely due to the fact that the particle size distribution is not exactly a Gaussian distribution.

In this paper, we concentrate on the exciton dynamics in QD's affected by an applied electric field. Figure 3 shows temporal responses of the exciton luminescence obtained at an emission energy $E=2.083$ eV together with the system response (indicated as laser) for (a) an electric field $F=2.1\times10^5$ V/cm and (b) $F=0$. Nonexponential decay is evident, as reported by several groups.[12–14] In fact, the exciton luminescence decay can be well described by a stretched-exponential function. The solid curves in Fig. 3 are the least-squares fit to the data using the stretched exponential function

$$I(t)=I_0\exp(-At^{\beta}), \tag{1}$$

where A is the decay rate and β is the decay exponent. Equation (1) fitted quite well for experimental data obtained in both conditions (in the presence or absence of an applied electric field). Stretched-exponential decay behavior can be expected from the relaxation of a distribution of decay lifetimes $G(\tau)$, so that the net behavior is a linear combination of the form $I(t)=\int G(\tau)e^{-t/\tau}d\tau$. The stretched-exponential decay observed here arises from the fact that the luminescence decay at a fixed emission energy E corresponds to a distribution of lifetimes

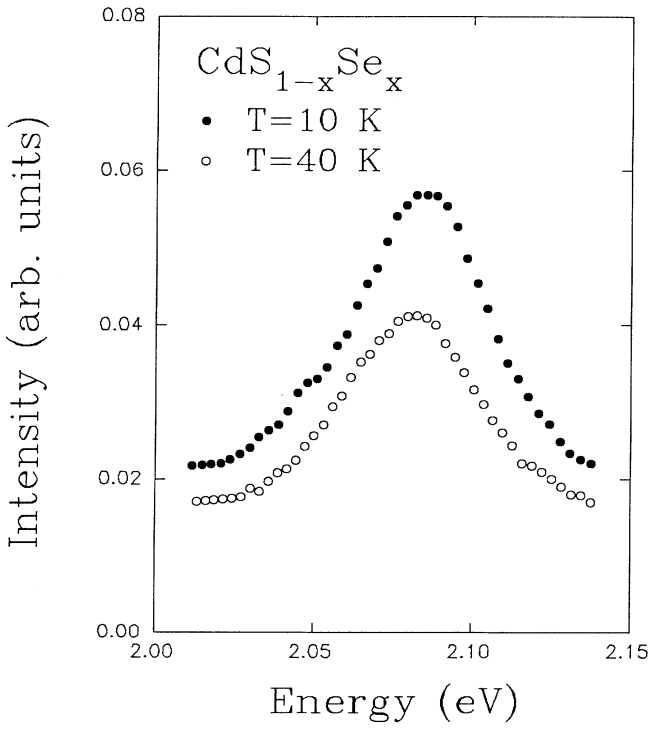

FIG. 2. Time-integrated exciton luminescence emission spectra of $CdS_{1-x}Se_x$ QD's embedded in a glass matrix obtained at $T=10$ and 40 K. For a clear presentation, spectra at different tempreatures have been rescaled, and the offset from zero intensity was given artificially.

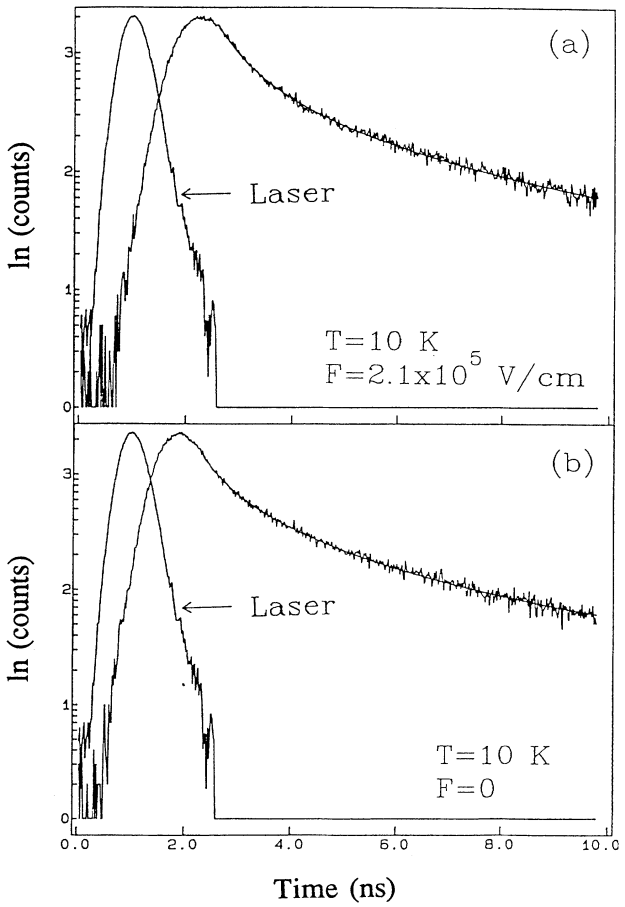

FIG. 3. Temporal responses of the exciton luminescence obtained at emission energy $E=2.083$ eV (a) in the presence of an electric field $F=2.1\times10^5$ V/cm and (b) in the absence of an electric field $F=0$. Each plot includes the system response (indicated as laser), experimentally measured luminescence decay, and the least-squares fit (solid curve) by using Eq. (1).

due to different sizes and compositions.

The decay rate A versus the applied electric field F obtained at $T=10$ K (● ● ●) is presented in Fig. 4. It shows that the decay rate decreases linearly with the field up to the maximum electric field used here (2.5×10^5 V/cm). The solid line drawn through the data points of the decay rate A in Fig. 4 is the least-squares fit by a linear equation, $A=A_0-\alpha_F F$. The fitted values are $A_0=4.77$ ns$^{-\beta}$ and $\alpha_F=(6.12\pm0.55)\times10^{-6}$ cm/ns$^{\beta}$V. We should point out that the field-induced reduction in the exciton decay rate observed in QD's here is much smaller compared with the same effect observed in the QW structures.[15,16] Figure 4 also shows the decay exponent β versus electric field F obtained at a temperature $T=10$ K (○ ○ ○). The decay exponent β increases linearly with the applied electric field. The solid line for β is the least-squares fit to the data using $\beta=\beta_0+\alpha_\beta F$. The fitted values are $\beta_0=0.21$ and $\alpha_\beta=(2.34\pm0.16)\times10^{-7}$ cm/V. The exponent β describes the dispersion in the decay rates. The results in Fig. 4 indicate that the distribution of the decay rates of the electron-hole pairs, which contribute to luminescence at an emission energy E, spreads out less under an applied electric field, which is expected. Under an applied electric field, the luminescence contributed by QD's in the tail of the size distribution becomes less probable, implying a smaller dispersion in lifetimes (larger values of β).

It was found from electroabsorption experiments that for small size QD's the electric-field-dependent Franz-Keldysh[5] oscillations were absent, and that the spectral shape was largely independent of the electric fields up to 10^6 V/cm. Due to the broad linewidth and small peak position shifting, it was difficult to observe directly any luminescence peak position shift under the electric field from the emission spectral measurements. The change of the luminescence emission spectrum due to the presence of an electric field is not noticeable within the experimental uncertainty. This implies that the decay rate change due to the spectral peak position shift with electric field is negligible.

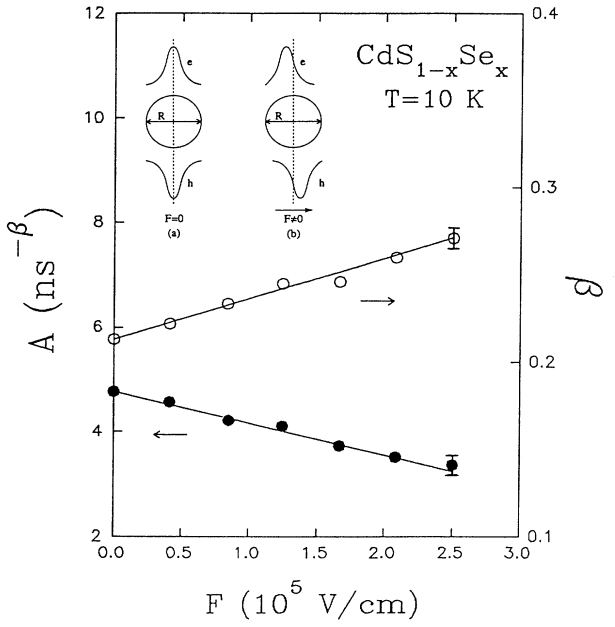

FIG. 4. The decay rate A (● ● ●) and decay exponent β (○ ○ ○) as functions of the applied electric field F at $T=10$ K. The solid lines are the least squares by linear equations. The inset shows the schematic diagram of electron (e) and hole (h) wave functions inside a spherical quantum dot of radius R in the absence of an applied electric field (a) and in the presence of an applied electric field (b).

The decrease of the exciton decay rate under an applied electric field can be understood by considering the electron and hole wave function overlap. By adopting the same picture from QCSE's in quantum wells,[16] an applied electric field can enhance the spatial separation between the confined electrons and holes in QD's. The inset of Fig. 4 shows a simple schematic diagram of the electron and hole wave functions in the presence or absence of an electric field. If the applied electric field is pointing to the right, the electron (hole) wave function will move toward the left (right), as shown in the inset. Therefore the electron and hole wave-function overlap will be reduced under an applied electric field, which results in a decrease of the decay rate. In general, the electron and hole wave functions outside the QD's are small, and the exciton decay rate under an electric field can be approximated by

$$A(F)=A_0\left|\int\Psi_e(r)\Psi_h(r)dr\right|^2, \tag{2}$$

where A_0 is the exciton decay rate in the absence of an electric field. Ψ_e (Ψ_h) is the electron (hole) wave function. The integral is the overlap of the electron and hole wave functions.

It can be shown easily that the exciton decay rate in QD's will have a quadratic field dependence $A(F)=A_0-\lambda F^2$ if one neglects the Coulomb interaction between the electron and hole and treats the potential barrier between the QD's and glass matrix to be infinitely high. Under the above two assumptions, the changes of wave functions of electrons and holes under electric fields are of exactly the same magnitude but of opposite signs, which will lead to quadratic field dependence of the decay rate. The linear field dependence of the decay rate observed here indicates that at least one of the above two assumptions is invalid. Especially for small QD's, the Coulomb interaction becomes very important.

Since only a linear dependence of the decay rate A on the electric field F is observed in the field region investigated, it implies that the system is in a weak-field regime for a field up to 2.5×10^5 V/cm, and so the perturbation method can be used. In the following, by including the difference between the electron and hole wave functions in QD's, we use a perturbation method to derive the linear field dependence of the decay rate. The perturbation Hamiltonian due to the electric field is

$$H'=eF(z_h-z_e), \tag{3}$$

where F is the field strength and z_e (z_h) is the z coordinate of the electron (hole). The electron and hole wave functions under an applied electric field F in the perturbation theory can be written as

$$\Psi_i = \Psi_i^{(0)} + \Psi_i^{(1)} = \Psi_i^{(0)} \pm C_i F \Psi_{in}^{(0)} \quad (i = e \text{ or } h) , \tag{4}$$

where

$$C_i = \frac{e \sum_{n \neq 0} \langle \Psi_{i0}^{(0)} | z_i | \Psi_{in}^{(0)} \rangle}{E_{i0}^{(0)} - E_{in}^{(0)}} \quad (i = e \text{ or } h) , \tag{5}$$

with $-$ ($+$) sign for electron (hole). $\Psi_{i0}^{(0)}$ and $\Psi_{in}^{(0)}$ ($E_{i0}^{(0)}$ and $E_{in}^{(0)}$) are the unperturbated electron ($i = e$) and hole ($i = h$) wave functions (energies) for the ground and nth excited states, respectively. The unperturbated electron and hole wave functions and energies are the solutions of the Schrödinger equation, which includes the Coulomb interaction between electron and hole and the corresponding boundary conditions. The exact solutions are not relevant for our purpose here. From Eqs. (2), (4), and (5), under an electric field, we thus obtain to the first order of F, the exciton decay rate

$$A(F) = A_0[1 - (D_h - D_e)F] , \tag{6}$$

with

$$D_i = 2e \sum_{n \neq 0} \langle \Psi_{i0}^{(0)} | z_i | \Psi_{in}^{(0)} \rangle \langle \Psi_{i0}^{(0)} | \Psi_{jn}^{(0)} \rangle / (E_{i0}^{(0)} - E_{in}^{(0)})$$

$$(i = e, j = h \text{ or } i = h, j = e) . \tag{7}$$

Because of the larger effective mass of a hole than an electron, the energy difference between the excited and ground states of the electron is larger than that of the hole, which results in $D_h > D_e$. The field dependence of the decay rate predicted by Eq. (6) is exactly what we observed experimentally, i.e., $A(F)$ decreases linearly with the applied electric field. The slope of A versus F shown in Fig. 3 equals the value of $A_0(D_h - D_e)$, where D_i ($i = e$ or h) can be calculated from Eq. (7) and $\Psi_{i0}^{(0)}$ ($\Psi_{in}^{(0)}$), the unperturbated electron (hole) wave function of the Schrödinger equation, by including the Coulomb interaction and spherical boundary conditions. This simple model does not give any indication concerning the photoluminescence energy peak position, i.e., whether or not the shift of the energy peak for the magnitude of electric fields applied in the experiment is detectable. The detailed calculation is in progress.

In conclusion, we have investigated the quantum-confined Stark effects of the exciton dynamics in CdS_xSe_{1-x} QD's. Under both conditions, either in the presence or absence of an applied electric field, we observe the stretched-exponential decay behavior of the exciton emission in QD's. The exciton decay rate and decay exponent have been measured, and a linear change with applied electric field up to 2.5×10^5 V/cm has been observed. The results have been accounted for by the field-induced reduction of the electron and hole wave-function overlap under an applied electric field. Further investigations of the size dependence of QCSE's in QD's will be carried out in the near future.

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