Exciton dynamics in a CdSe/ZnSe multiple quantum well

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We use time-resolved spectroscopy to study exciton relaxation at 10 K in a CdSe/ZnSe multiple quantum well that exhibits well-thickness fluctuation. Three distinct relaxation processes contribute to the time evolution of the luminescence. The first is the localization of excitons into local band-gap minima with a time constant ~4 ps, which includes hot-exciton formation and cooling. The second process is the migration of localized excitons between local minima, which is a tunneling process accompanied by phonon emission; it cannot be described by a single time constant and strongly depends on energy. The final contribution to the process is the recombination of localized excitons with a time constant ~470 ps.

Exciton dynamics in semiconductor quantum wells (QW's) have been studied intensively in recent years. In high-quality QW's, which are characterized by homogeneous broadening and zero Stokes shift in optical spectra, it is understood that intrinsic excitons dominate the relaxation processes.[1–4] The photoexcited electron-hole pairs emit phonons to form hot excitons with large in-plane wave vector $\mathbf{K}_{\|}$. The hot excitons interact among themselves and with phonons, and relax to $\mathbf{K}_{\|}\approx\mathbf{0}$ excitons which then recombine radiatively. In QW's with interface steps, inhomogeneous broadening and a Stokes shift characterize the optical spectra. Excitons in such QW's have not only kinetic energy, but also potential energy which varies following the in-plane band-gap fluctuation which is in turn controlled by the local well thickness. Apart from the momentum relaxation, excitons may also move in response to the force due to the spatial variation of the potential energy. An exciton may be localized in a local band-gap minimum within its lifetime.[5–7] In addition to the above-mentioned relaxation processes for intrinsic excitons, localization of excitons from hot or $\mathbf{K}_{\|}\approx\mathbf{0}$ delocalized excitons, and the migration of localized excitons between local minima complicate the exciton dynamics. Previous studies[5,8–12] demonstrated clearly the migration of localized excitons. However, there is not a satisfactory study dealing with both the exciton localization and the localized exciton migration. Localization of excitons is different from the localization of the electronic states in a disordered solid. This is because an exciton is a quasiparticle with finite lifetime, and the localization of an exciton is therefore determined by whether it is movable within its lifetime. A common convention has proved useful for defining a localized exciton:[6,9,13] a $\mathbf{K}_{\|}\approx\mathbf{0}$ exciton is called localized when its center-of-mass wave function is centered at a point in the QW plane where it has minimum potential energy with respect to its surrounding area (local minimum). It has been shown[13] that the distribution of localized exciton states is close to a Gaussian distribution in QW's with random monolayer fluctuations, and *not* an exponential distribution with a mobility edge as is that of the localized electronic states. Excitons situated at a local minimum may migrate to other local minima of lower energy by tunneling accompanied by phonon emission[5,11,14] or thermally activated processes.[15]

The dynamics of excitons in wide-band-gap II-VI QW's, especially the localization, is of particular interest since laser emission is due to the recombination of localized excitons.[16] Previous studies[11,16] did not experimentally measure the localization time of excitons in II-VI QW's because of the limited temporal resolution in these experiments. In this paper, we present a femtosecond photoluminescence measurement of a CdSe/ZnSe multiple QW with monolayer fluctuations. By using the above-mentioned concept of the localized exciton to analyze the luminescence evolution across the inhomogeneously broadened peak, we measure successfully the localization, migration, and decay of the exciton.

The sample used in this study was a 100-period 1-nm CdSe–5-nm ZnSe multiple quantum well. The cw luminescence and absorption spectra of this sample show inhomogeneous broadening over 100 meV in linewidth (full width at half maximum), which corresponds to a ± 1 ML fluctuation in QW thickness. One result of the large inhomogeneous broadening is that the thermalization[15] of localized excitons can be ignored at low temperature. The 4050-Å second harmonic of a mode-locked Ti:sapphire laser was used as the excitation source for time-resolved measurements. The autocorrelation width of the laser pulse is 100 fs, and that of its second harmonic is 300 fs. The excitation density of *e-h* pairs in the QW is less than 3×10^{10} cm^{-2}. Time-resolved luminescence spectra were measured using the frequency upconversion technique[17] and achromatic collection optics. The temporal resolution of the whole system is ~300 fs determined by the pulse width of the second harmonic. The upconversion signal was focused into a $\frac{1}{4}$-m monochromator with 18-meV spectral resolution determined by the natural width of the laser pulse. The final signal was detected by a cooled photomultiplier tube with a photon counter. Data were accumulated either as spectral scans at fixed time delays or as time scans at fixed spectral positions.

The photon energy of the laser excitation, 3.1. eV, is chosen to be larger than the band gap of the ZnSe confinement layer and much larger than ground-state energies of excitons

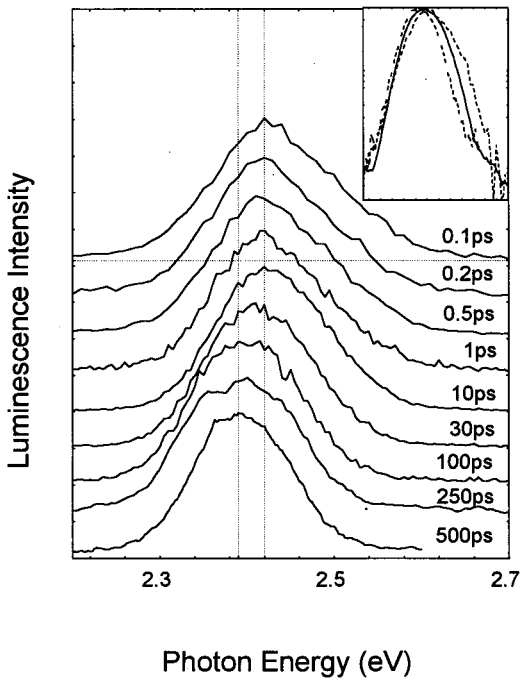

FIG. 1. Photoluminescence spectra at 10 K at different times after excitation. The intensities are normalized and base lines are shifted for clarity. The inset shows the spectra measured at 0.1, 100, and 500 ps after excitation on a logarithmic intensity scale.

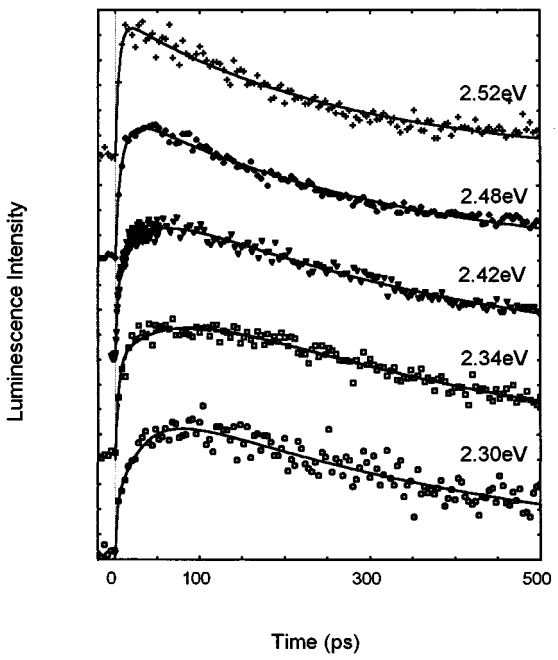

FIG. 2. Time evolution of photoluminescence measured at different photon energies. Symbols are experimental data. Solid curves are the least-squares fit using Eq. (5). Intensities are normalized and base lines are shifted for clarity.

in the QW. This means that photoexcited electron-hole pairs will populate the QW's according to the distribution of local well widths. In contrast, near-resonant and resonant excitation may create excitons preferentially in some QW sites with a particular well thickness, which give extra terms in a description of the luminescence line shape, and/or cause LO-phonon-assisted tunneling of excitons within the inhomogeneously broadened photoluminescence band which show additional sharp peaks in the spectrum.[11,18]

Figure 1 shows the luminescence spectra at different delays after excitation. The peak intensities are normalized and the base lines are shifted for clarity. For the first 1 to 10 ps, the luminescence spectra have almost the same shape and peak position. From 10 to 100 ps, the luminescence peak redshifts by about 30 meV, and the shape of the spectrum also changes. The high-energy side of the luminescence peak decreases faster than the low-energy side, as shown more clearly in the inset of Fig. 1. For delays greater than 100 ps, both the peak position and the width of the spectrum showed little further change. The time evolution of the luminescence intensity was measured at 2.30, 2.34, 2.42, 2.48, and 2.52 eV. Each data set was taken from -20 to 500 ps at 5-ps intervals. These decays are shown as symbols in Fig. 2, with base lines offset and the maximum intensities normalized for clarity. The rise of the luminescence is also measured at the peak position 2.42 eV from -5 to 50 ps with 0.5 ps per step. The decay curve for 2.42 eV in the figure combines data from both sets of measurements. It can be seen that the two data sets join smoothly, confirming the reliability of the experiment. The common feature for all photon energies is that the luminescence intensity follows a rapid rise in the first few picoseconds. Following the rapid rise, the luminescence intensity changes differently at different energies. For the data measured at 2.52 eV, the intensity decreases exponentially. For other photon energies, as the photon energy decreases the rapid rise of luminescence turns into a slower rise before it falls off exponentially. The slow rise time increases with decreasing photon energy. The decay of the luminescence intensity follows a similar rule.

Comparing Figs. 1 and 2, we obtain a clearer picture of the exciton relaxation. During the fast rise in luminescence intensity—from 0- to ~10-ps delay—the spectral shape retains the same form. For longer times, the redistribution of the excitons in the inhomogeneously broadened band of states causes a shift of the emission towards lower energies. The loss of excitons from the high-energy states also leads to a narrowing of the emission spectrum. These results are very similar to those reported by Masumoto, Shionoya, and Kawaguchi[5] for a GaAs multiple quantum well (MQW) sample, though the inhomogeneous broadening in that case is over an order of magnitude smaller than that in the present work.

We now present an exciton relaxation model to describe the above experimental results. The important relaxation processes involved in the exciton dynamics include the following: first, photoexcited hot carriers emit phonons to form hot excitons with large in-plane wave vector.[19] Hot excitons may be formed in QW's or in the confinement layers. Second, hot excitons lose kinetic energy by emitting phonons and eventually form excitons with $\mathbf{K}_{\parallel} \approx \mathbf{0}$. While excitons lose kinetic energy, they are also driven by the gradient of the potential energy between the QW and confinement layers in searching for low potential energy sites. As a result, excitons with $\mathbf{K}_{\parallel} \approx \mathbf{0}$ accumulate in QW's rather than in the confinement

layers. This argument is justified by the fact that luminescence from confinement layers is much weaker than from the wells in most MQW samples. By the same token, excitons are also driven by the gradient of the in-plane potential energy towards band-gap minima during their momentum relaxation. Eventually, all excitons with $\mathbf{K}_{\parallel}\approx\mathbf{0}$ should be found at local minima in QW's. This leads to the argument[7,13] that luminescence is due to the recombination of localized excitons. Third, excitons may migrate in and out of local minima in searching for lower energy sites by emitting phonons. Fourth, localized excitons radiate into photons. The time evolution of the luminescence is determined by these relaxation processes: because they occur on different time scales, the luminescence within a certain time range may only be determined by one or two of these processes. In addition to the above-mentioned relaxation, electrons and holes may not form excitons if they are trapped at different local minima with a large separation.[20,21] The dynamics of recombination of ''nongeminate'' electrons and holes is on a much longer time scale, beyond the time range of our measurements. It will not be discussed here.

The above analysis may be quantified by a rate equation. We will use the hypothesis that the first two processes are much faster than the latter two. Moreover, since the time resolution of our system is not able to measure and distinguish exciton formation, cooling, and localization, we will use a *single* time constant τ_1 to describe these processes taken together. The migration of a localized exciton will be described by $1/\tau(E_1,E_2)$, the migration rate from states of energy E_1 to those of E_2. Finally, the radiative recombination can be described by a *single* time constant τ_r across the inhomogeneously broadened luminescence spectrum. In addition, the exciton migration to higher energy is assumed to be negligible at low temperature. The rate equation for the time-related distribution of localized excitons $f(E,t)$ can then be written as

$$\frac{df(E,t)}{dt}=G(E,t)+\int_{E}^{E_{\max}}\frac{f(\varepsilon,t)}{\tau(\varepsilon,E,t)}\,d\varepsilon-\frac{f(E,t)}{\tau_r}-\int_{E_{\min}}^{E}\frac{f(E,t)}{\tau(E,\varepsilon,t)}\,d\varepsilon, \tag{1}$$

where $\int_{E_{\min}}^{E_{\max}}f(E,0)dE=1$, and $f(E,0)$ is the distribution of localized states.[13] The first term on the right-hand side of the equation describes the formation of localized excitons by hot carrier or hot-exciton cooling. It is proportional to the distribution function of localized states $f(E,0)$. The second and last terms are, respectively, the migration rate into and out of localized exciton states with energy E. $E_{\max}$ and $E_{\min}$ represent the upper and lower energy limits of localized excitons, determined by the largest and smallest local well widths. The third term describes the recombination. The density of the exciton population at t and within the energy interval ΔE can then be written as $n_0 f(E,t)\Delta E$, where n_0 is the density of photoexcited carriers at $t=0$. A similar rate equation has been derived by Takagahara [Eq. (7) in Ref. 6] without considering the direct generation of localized excitons $G(E,t)$, where $\tau(E_1,E_2)$ was described explicitly in terms of exciton-acoustic phonon interactions. To solve (1) numerically one needs to know not only the distribution of local minima, but also distributions of the depth, the size of local minima, and the distance between them. This is itself an unsolved problem. In addition, the solution of these equations requires many parameters, some of which have to be assumed. In order to compare our experimental results with the data, we decompose (1) into three population rate equations, which can be solved analytically. The first equation describes the hot carrier cooling. If the laser pulse is much shorter than the carrier cooling time, hot carriers are created instantly with the same energy after excitation. If we ignore the thermalization of hot carriers and hot excitons, the relaxation of hot excitons can be treated as a two-level system of hot exciton and localized exciton. Then,

$$\frac{dn_h}{dt}=-\frac{n_h}{\tau_1}, \tag{2}$$

where n_h is the density of hot excitons. At $t=0$, $n_h=n_0$ equals the carrier density created by photoexcitation. In the second equation, we treat the localized excitons above energy E as if they are in a single level,

$$\frac{d\langle n_1\rangle}{dt}=F(E)\frac{n_h}{\tau_1}-\frac{\langle n_1\rangle}{\tau_r}-\frac{\langle n_1\rangle}{\tau_{m1}} \tag{3}$$

where $\langle n_1\rangle=n_0\int_{E}^{E_{\max}}f(E,t)dE$ is the density of excitons from E to $E_{\max}$; $F(E)=\int_{E}^{E_{\max}}f(E,0)dE$. Because there are no localized excitons above $E_{\max}$, the second term in (1) does not appear in (3). The last term corresponds to the migration of localized excitons into lower energy states, $1/\tau_{m1}=\int_{E}^{E_{\max}}[1/\tau(\varepsilon,E,t)]dE$. The third equation is a modification of (1),

$$\frac{dn(E,t)}{dt}=f(E,t)\frac{n_h}{\tau_1}+\frac{\langle n_1\rangle}{\tau_{\mathrm{mi}}}-n(E,t)\left(\frac{1}{\tau_r}+\frac{1}{\tau_{\mathrm{mo}}}\right), \tag{4}$$

where $1/\tau_{\mathrm{mi}}$ is the migration-in rate from $\langle n_1\rangle$; $1/\tau_d$ is the total decay rate including the recombination rate $1/\tau_r$ plus the migration-out rate $1/\tau_{\mathrm{mo}}$ from E into lower energies, while the recombination rate includes both the radiative and nonradiative contributions. From (1), the second term in (4) is mathematically incorrect. Because $f(\varepsilon,t)$ in the second term in (1) cannot be taken out of the integral, the migration-in of excitons cannot be described by a single time constant. Therefore τ_{mi} does not relate to any real physical process. We assume this will not much affect the solution of (2)–(4) for τ_1 and τ_d if τ_{mi} is of a different order of magnitude. Since the luminescence intensity $I_{\mathrm{lum}}(E,t)$ is proportional to $n(E,t)$ at energy E, the solution of (4) can be compared directly with the experimental data. By assuming $\tau_1 \ll \tau_{m1} \ll \tau_r$, we obtain

$$I_{\mathrm{lum}}(E,t)\propto\{[\exp(-t/\tau_r-t/\tau_{\mathrm{mo}})-\exp(-t/\tau_1)]+C[\exp(-t/\tau_r-t/\tau_{\mathrm{mo}})-\exp(-1/\tau_r-t/\tau_{m1})]\}. \tag{5}$$

The above expression has five parameters; four time constants describe the exciton localization, migration, and recombination, respectively; the coefficient C is a function of $f(E)$, $F(E)$, τ_1, and τ_{mi}. Because the second term in (4) has

TABLE I. Time constants obtained using Eq. (5).

Photon energy (eV)	Localization time τ_1 (ps)	Decay time τ_r (ps)	Migration-out time τ_{mo} (ps)	Migration time τ_{m1} (ps)
2.30	4.0	466	9262	40.4
2.34	4.0[a]	468	3858	76.6
2.42	4.0	476	2030	43.9
2.48	4.0	494	939	12.3
2.52	4.2	472	610	20.3

[a]This value is fixed in the fitting. By varying τ_1 the least squares fit gives τ_1, 6.6 ps and τ_r, 405 ps.

been modified, the migration time τ_{m1} is not the same as the one in (3). It does not relate to a real process.

In Fig. 2, curves represent the least-squares fit of (5) to the experimental data. It is no surprise that the agreement between the formula and the data is very good since five fitting parameters are used. However, the consistency of the fitting parameters for different photon energies suggests that our model is a very reasonable one: the values are listed in Table I. In deriving (5), we assumed $\tau_1 \ll \tau_{m1} \ll \tau_r$. Comparing the three time constants in Table I, we find such an assumption justified. Since these time constants are very different in magnitude, each of them should dominate the time evolution of the luminescence in a certain time range. This also confirms that the modification made in (4) should not affect τ_1 and τ_r much.

The fast rise of the luminescence is determined by the exciton localization time τ_1. It is almost a constant within the experimental error for all photon energies, as shown in column 2, just as our model predicted. The value of about 4 ps accounts for the hot-exciton formation and hot-exciton relaxation. It is much faster than the reported hot-exciton formation and cooling in an *intrinsic* GaAs QW.[2] The *single* localization time implies the possibility of a tunable laser diode of II-VI QW's, provided that laser emission is due to the recombination of localized excitons. The recombination times at different energies are also almost a constant at about 470 ps (column 3), which also agrees with the prediction of our model.

The migration-out time τ_{mo} increases rapidly with decreasing photon energy as shown in column 4. This is so because at low energy, there are fewer localized states available to lower energy and it is therefore more difficult for excitons to migrate out. Because the total decay rate of the luminescence intensity is the sum of the recombination rate $1/\tau_r$ and the migration-out rate $1/\tau_{\mathrm{mo}}$, the fast migration-out rate $1/\tau_{\mathrm{mo}}$ at the high-energy part of the luminescence spectrum leads to a faster apparent decay rate, while the low-energy part of the spectrum decays at a rate close to the recombination rate. Eventually, the whole luminescence spectrum shifts to lower energy and its width narrows. After 100 ps, the temporal evolution of the band is dominated by the recombination decay.

The slow rise of the luminescence is due to the migration-in of localized excitons. It requires the exact solution of (1). However, the phenomenological value τ_{m1} explains why the spectral redshift and narrowing were observed from 10 to 100 ps after excitation.

The similarity between this result in a CdSe-ZnSe QW and that in GaAs QW's in Ref. 5 suggests a universality of the localized exciton migration. Whether this process is important in a certain system depends on the relative order of the time constants. For example, if the localization time is much larger than both the hot-exciton cooling time and the recombination time, there should be no exciton localization. The Stokes shift observed in cw photoluminescence is then due to the thermalization of excitons.[15] On the other hand, comparing the luminescence rise time in an intrinsic QW and in a QW with layer thickness fluctuation will reveal how the field induced by the potential fluctuation affects the hot-exciton cooling.

In summary, we have measured time-resolved spectra of CdSe-ZnSe multiple QW's with 300-fs time resolution which allows us to observe clearly the evolution of exciton luminescence. Exciton relaxation was modeled by exciton localization, localized exciton migration, and recombination. The exciton localization time is about 4 ps, which is much faster than the recombination time, while the migration time of localized excitons depends on energy and could be much larger than the recombination time.

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