Quantum Dot Exciton Dynamics through a Nanoaperture: Evidence for Two Confined States

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Excitons confined to CdSe/ZnSe self-assembled quantum dots are probed through a nanoaperture using time-resolved photoluminescence. Significant evidence is shown that *two* different electronic states are associated with these dots, with binding energies which differ by an order of magnitude. The first has a short 450 ps lifetime, exhibits a relatively broad emission line, and persists nearly to room temperature; the second exhibits a long (>4 ns) lifetime and is responsible for the sharp (~ 100 μeV) lines seen at low temperatures (<60 K). These results are completely unlike those seen in III-V dots, and reveal the complexity of the electronic structure in CdSe dots.

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The past decade has seen a surge of effort in developing methods for confining electronic states in semiconductors to less than two dimensions. One of the most effective methods has been the growth of self-assembled quantum dots (SAQDs) which are formed when the large lattice strain between two different semiconductor layers is relieved to form well-defined pyramids or domes across the epitaxially grown surface; examples are InAs on GaAs [1], or more recently, CdSe on ZnSe [2–4]. Many experiments over the past six years have shown that these structures strongly confine electrons and holes, and result in nearly a zero-dimensional density of states. More recently, intense efforts have been directed toward understanding the *internal* electronic structure of these quantum dots (QDs), and how this structure changes with the various material systems. Theoretical calculations which include the effects of strain on these structures have shown that the confined electronic states can be quite complex, with electrons or holes separately confined to regions on the perimeter or interior of the quantum dots [5].

In this Letter, we present temporally and spatially resolved photoluminescence (PL) experiments on CdSe/ZnSe self-assembled quantum dots which show directly that there are two different types of electronic states associated with these QDs with radically different binding energies and electron-hole wave functions. Moreover, these results show clearly that the character of these electronic states is significantly different than has been observed in the InP/InGaP or InAs/GaAs QD systems.

Because of its sensitivity to electron and hole wave function overlap, time-resolved (TR) photoluminescence can be a powerful tool for probing the internal electronic structure of QDs. A number of macro-PL measurements on a >30 μm length scale have shown approximately 0.5–1 ns lifetimes which are weakly temperature dependent [6–11]. More recently, Zwiller *et al.* have shown spatially and temporally resolved μ-PL of InP/GaInP QDs which displayed relatively sharp (3 meV wide) spectral features [12]. However, these experiments also did not show significant distinction in the lifetimes of the different spectral features.

In this Letter, we report the first measurement of time-resolved PL through a 200 nm aperture which shows directly the dynamics associated with the ultrasharp 200 μeV spectral features associated with zero-dimensional confinement. More importantly, we show *two* distinctly different types of temporal behavior for emission from these II-VI QDs. The first, which exhibits a 450 ps lifetime, is spectrally broad and *not* associated with the sharp spectral emissions. We find that the lifetime of the sharp 200 μeV emission lines is an *order of magnitude* longer, with a lifetime estimated to be greater than 4 ns. Moreover, we also find that the temperature dependence of these two spectral features also are significantly different. These results provide a window into the internal complexity of the electronic states in these QDs.

The CdSe dots are grown using molecular beam epitaxy (MBE), with strained island formation resulting from the well-known 7% lattice mismatch between ZnSe and CdSe [2–4,9,13,14]. The samples were fabricated in a Riber 32 R&D MBE machine equipped with elemental sources. First, approximately 1 μm of ZnSe was grown at 300 °C on a (100) GaAs substrate. Second, three monolayers of CdSe were grown at a slow rate of 0.025 monolayers per second to ensure controlled deposition. Finally, the sample was capped with a 50 nm thick layer of ZnSe.

Much less is known of the CdSe SAQDs grown on ZnSe than for the InAs system; the growth mechanisms and structure of the CdSe SAQDs are clearly different than seen for InAs dots [2,13,15,16]. The CdSe quantum dots are approximately 10 nm in diameter and 3 nm in height, and occur at a density of approximately 100 to 500 dots/μm^2 [17]. The electronic states in these II-VI structures are expected to be significantly different than in the III-V dots because of the larger exciton binding

energies, enhanced electron-hole exchange interaction, and stronger electron-phonon coupling [6,18–20].

A number of cw optical experiments have sampled macroscopic regions (~30 μm diameter) of the CdSe QD samples and have exhibited a wide photoluminescence line (~75 meV), reflecting an inhomogeneous distribution of the thousands of CdSe dots sampled [2,15]. This PL line is quite intense at low temperatures and persists to nearly room temperature [2,15]. Several time-resolved macro-PL experiments have exhibited a *single* decay lifetime of 300 to 500 ps which persists to high temperatures [6–9].

As one studies smaller areas of the CdSe quantum dot samples, using μ-PL (<2 μm) or nano-PL (<200 nm), many sharp lines (100–200 μeV) appear superimposed over a broad emission line [3,6,9,15,19,21,22].

To observe the dynamics of a few quantum dots, we collect PL through a fixed 200 nm diameter nanoaperture. The nanoaperture is produced by using 200 nm monodispersed polyspheres as shadow masks. After deposition of a silver thin film, the spheres are washed away, leaving a random array of high-quality 200 nm apertures. The excitation is provided by 200 fs pulses at 430 nm emitted from a frequency-doubled mode-locked Ti-sapphire laser every 12.7 ns. The PL is dispersed through a 3/4-m single spectrometer and detected by a Hamamatsu 943 GaAs photomultiplier tube. The spectral resolution of the system is 150 μeV, and the system time response is 500 ps. Figure 1 shows normalized time-resolved spectra over a small 5 meV energy range obtained through a nanoaperture at 2 K; the 5 meV range is on the low energy side of the macro-PL peak. These spectra show four distinct, sharp 150 μeV lines which persist for more than 4 ns after the laser pulse. In addition, a poorly resolved broad emission line, which decays quite rapidly, underlies these sharp features.

From these time-resolved spectra we extract the intensities of the sharp peaks and the broad emission. The intensities of the broad and sharp emissions are plotted as a function of time in Figs. 2(a) and 2(b), respectively. One can see directly that each of the exciton states responsible for the four narrow 150 μeV lines exhibits a long 4 ns lifetime, while the state responsible for the broad emission decays rapidly in less than 1 ns.

The fact that the exciton states responsible for the broad and sharp emission lines exhibit dramatically different lifetimes suggests that the overlap of the electron and hole wave functions must be very different. To see if this difference is reflected in the effective binding energy of these two states, we average over *many* quantum dots and look at the lifetimes of these two states as a function of temperature. The doubled Ti-sapphire laser is focused to a 30 μm diameter spot on the sample. The PL is dispersed by a 3/4-m single spectrometer and detected by a fast microchannel plate photomultiplier tube with a

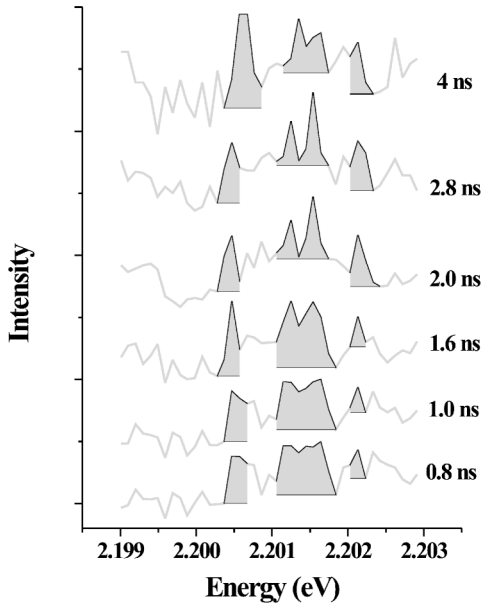

FIG. 1. Time-resolved and spectrally resolved nano-PL from a sample with an aperture of 2 K. Sharp (~150 μeV) features persist (see shaded regions) from 0.8 to 4.0 ns, indicating that excitons confined to the dots are long lived.

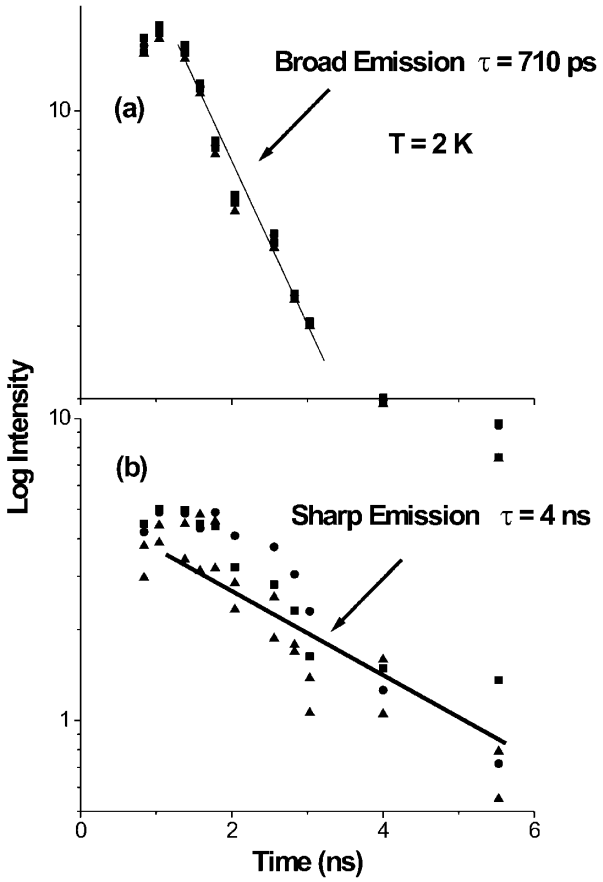

FIG. 2. The logarithmic intensity versus time of the (a) broad emission and (b) sharp features, as determined from the time-resolved data shown in Fig. 1. Note the presence of two distinct lifetimes.

system time response of 80 ps. Figure 3(b) shows time decays taken at the peak of the broad emission which display a double exponential behavior with two distinct lifetimes (450 ps and 4 ns), which again differ by an order of magnitude [23]. Both decay times are found to be approximately temperature independent up to 100 K. The *intensity* of the long-lived state, however, decreases monotonically with temperature and disappears by 60 K; the short-lived state persists up to room temperature. This suggests that the long-lived state responsible for the sharp emissions is much more weakly bound than the short-lived state.

This difference is also reflected in temperature-dependent μ-PL. In Fig. 3(a) we show μ-PL measurements of the CdSe quantum dots for several temperatures. The sample is placed inside a continuous flow cryostat, with the 476 nm line from a cw Ar-ion laser focused to a 1.7 μm diameter spot on the sample surface. These spectra immediately reveal the presence of two different types of states. The 6 K spectrum shows a broad 50 meV line, over which are imposed many spectrally sharp lines with an average linewidth of 200 μeV [21,22]. The sharp lines quench by 60 K, leaving a broad PL feature which persists to room temperature. Extensive nano-PL [22] through a 200 nm aperture on this sample has shown that *individual* 200 μeV lines can be followed as a function of temperature and quench by 60 K. This indicates that the broad spectral feature (which persists to room temperature) is *not* composed of unresolved narrow spectral features.

To estimate the effective binding energies of these two states, we show in Fig. 4 the normalized intensities of the broad (gray triangles) and sharp (gray circles) spectral features from μ-PL spectra [Fig. 3(a)] as a function of inverse temperature. The intensities obtained from fits of the double exponential decays in Fig. 3(b) shows that the short-lifetime component corresponds to the broad emission feature, while the long-lifetime component corresponds to the sharp spectral features. Moreover, these intensities are successfully modeled with the activated behavior,

$$I(T) = I_0/[1 + C\exp(-\Delta E/k_B T)]. \quad (1)$$

The solid lines are fits to each of these states, where ΔE is 4 meV for the sharp emission states and ΔE is 42 meV for the broad emission states [22]. This shows that there are *two types* of emission associated with these quantum dots, whose activation energies differ by an order of magnitude.

These spatially and temporally resolved PL measurements, taken together, provide compelling evidence for *two distinct states* which are responsible for emission from the self-assembled CdSe quantum dots. The sharp

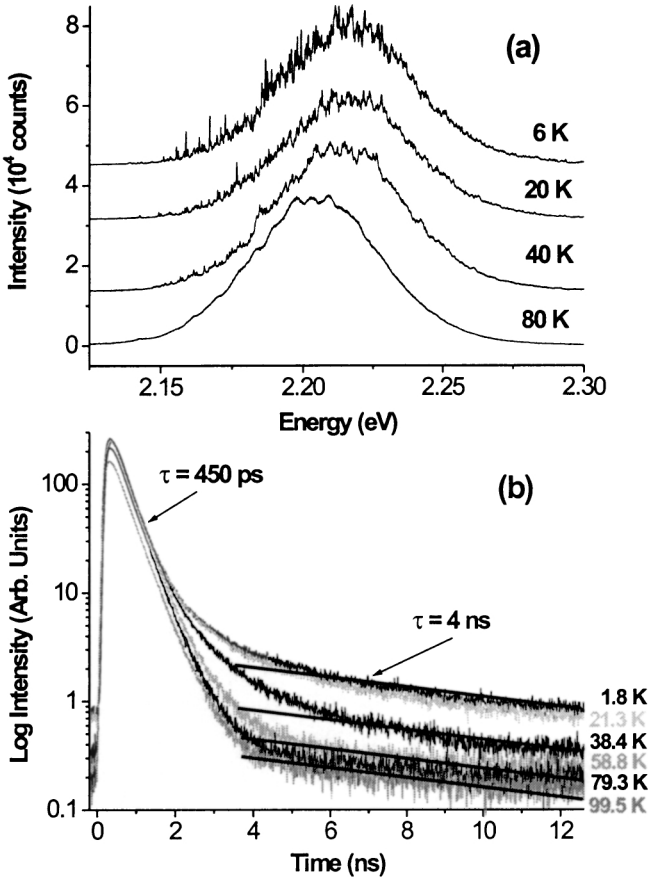

FIG. 3. (a) μ-PL spectra at four different temperatures. The 6 K spectrum displays a broad peak over which many sharp emission lines are superimposed. Note that these sharp emission lines disappear above 60 K. (b) Macro-PL time decays at the peak energy of the broad emission for several temperatures. Two distinct exponential decays can be seen, one with $\tau = 450$ ps and a second with $\tau = 4.0$ ns. The long-lived component vanishes by 60 K.

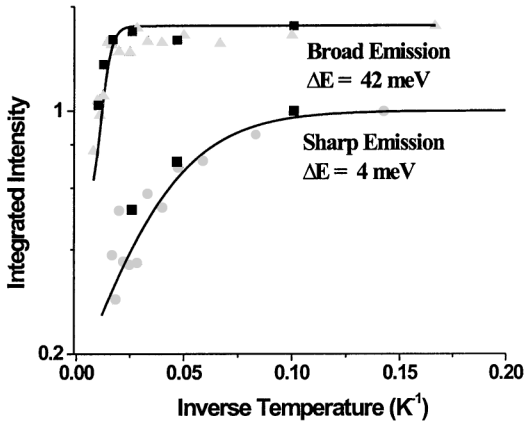

FIG. 4. The spectrally integrated intensities from both cw μ-PL and time-resolved data plotted as a function of inverse temperature. The gray triangles and circles are the cw data for the broad emission and sharp emissions, respectively. The black squares are the TR data for both the short- ($\tau = 450$ ps) and long-lived ($\tau = 4.0$ ns) decays. The solid lines are fits to combined data for each of the two states using Eq. (1) which show activation energies of 4 and 42 meV.

features clearly result from excitons confined to the quantum dots. However, this state is only weakly bound (4 meV) and thermally depopulates by 60 K. The extraordinarily long lifetime of this state (4.0 ns) indicates that the overlap of the electron and hole wave functions is significantly weaker than for the short-lived state, suggesting that this excitonic state may result from spatially indirect electron-hole transitions.

In contrast, these spectra and lifetimes indicate that the state responsible for the broad emissions is strongly bound (42 meV) and persists nearly to room temperature. Moreover, the short lifetime of this second state indicates that the electron and hole overlap is large. However, significant uncertainties remain for the origin of the broad spectral feature. Preliminary optical transport measurements suggest that the broad spectral state is also localized, consistent with a picture of excitons confined to the quantum dots [24].

If both spectral features (broad and sharp) are emissions from excitons confined to the dots, then this implies that these CdSe SAQDs have a number of excitonic bound states with significantly different wave functions. The size of the QDs ($\sim 10-30$ nm) is significantly larger than the exciton Bohr radius (~ 5 nm) in CdSe, so that a number of bound states should be possible in each quantum dot. In addition, the internal distribution of strain in these dots is expected to be inhomogeneous and should have an important effect on the confining potential of the holes and electrons. For example, Zunger and coworkers have shown that the internal strain of InAs dots causes a minimum of the valence band potential along the outer perimeter of the dots, while the electrons remain predominantly confined to the interior of the dot [5].

In summary, high spatial resolution temperature- and time-dependent spectra of excitons confined to CdSe quantum dots strongly suggest the existence of two distinct states. The binding energies and radiative lifetimes of excitons in these two states differ by an order of magnitude, shedding important new light on the rich internal electronic structure of these quantum dots.

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