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Origin of two types of excitons in CdSe dots on ZnSe

S. Lee
Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556

J. C. Kim and H. Rho
Department of Physics, University of Cincinnati, Cincinnati, Ohio 45221-0011

C. S. Kim
Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556

L. M. Smith and Howard E. Jackson
Department of Physics, University of Cincinnati, Cincinnati, Ohio 45221-0011

J. K. Furdyna and M. Dobrowolska
Department of Physics, University of Notre Dame, Notre Dame, Indiana 46556

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Recent micro-PL and time-resolved PL data performed on CdSe dots embedded in ZnSe show compelling evidence that the PL emission results from two different kinds of states. We propose a model explaining the origin of these different states coexisting within a single dot. The main concept of the model is that, while the ground state of the heavy hole is confined to strain-induced potential pockets at the bottom of the island, the electrons and the first excited state in the valence band are distributed within the entire island. That difference in the degree of localization between the two heavy-hole band states is responsible for the different properties of PL transitions observed in our experiments.

Considerable progress has recently been made in the understanding of growth mechanism and electronic properties of self-assembled semiconductor quantum dots. For example, it was shown that the unavoidable presence of strain in these dots significantly affects the electronic structure of the confined states.[1–3] For the specific cases of InAs[1,2] and InP[3] dots the calculations show that the strain is inhomogeneous within the interior of a covered dot, and that it affects the band profile of the valence band by forming local minima (potential ''pockets'') in the region(s) of highest strain and—if the pockets are sufficiently deep—causing the holes to be confined there. In the conduction band, however, the electron wave function should be distributed (more or less symmetrically) throughout the *entire* island owing to the much lighter electron mass.

Such modification of the band profile should automatically affect the optical properties of these structures. In the case of InAs/GaAs QD system, however, the interpretation of optical spectra does not require invoking the band structure proposed in Refs. 1 and 2, nor does it depend on the existence of the electric dipole implicit in the fact that the centers-of-mass of the electron and the hole wave functions no longer coincide in this picture. Instead, the optical data observed on the InAs/GaAs system suggest that only one excitonic state is responsible for the PL emitted from each individual dot (appearing as a sharp spike in the micro-PL spectrum), and that the inhomogeneously broadened line observed in macro-PL is simply a superposition of such ultranarrow spikes.

In this paper we will show that the optical data which we observe on CdSe QDs embedded in ZnSe cannot be explained without invoking a band structure similar to that calculated in Refs. 1–3. That is, we argue that the strain-induced local potential minima at the base of the CdSe island are sufficiently deep, and the heavy hole masses are sufficiently heavy to localize the ground state of the heavy holes near those minima.

In order to perform a realistic band structure calculation applicable to the CdSe/ZnSe system—including its strain-induced modifications—it is essential to accurately reproduce the strain profile within the CdSe QD. This in turn requires knowledge of the *exact* geometry of the QD—a major problem, since the size and shape of these islands (both of which are strongly material- and growth-condition-dependent) are not precisely known. Furthermore, although the existing TEM data do not allow us to infer a specific shape for the covered CdSe islands, they do indicate that there is considerable interdiffusion in this system, and the dots actually consist of ZnCdSe *alloy* rather than CdSe, with an uneven Cd distribution throughout the dot.[4,5] The information on the strain distribution (which will automatically depend on Cd distribution) is therefore insufficient to allow a reliable band structure calculation. At this point one should note—as shown by Williamson and Zunger,[2] who carried out calculations for pyramidal and spherical InAs QDs embedded in GaAs—that the lower symmetry of the pyramidal dot produces a much richer strain profile than the spherical dot. Therefore one can expect that any realistic geometry of CdSe/ZnSe QDs (i.e., one involving a non-symmetric shape and composition profile) will lead to an even more complex strain distribution than that calculated for (pure) InAs dots of pyramidal shape[1,2] and (pure) InP dots with a truncated py-

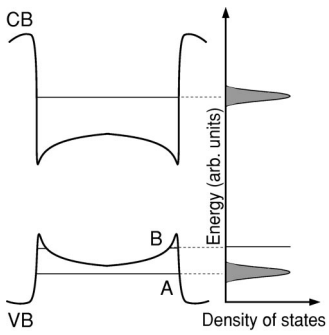

FIG. 1. Band alignment along a line passing through the base of the island. The diagram is based on detailed calculations (which include strain) by Pryor *et al.* for InP/GaInP quantum dots.[3] The right panel shows the density of states for the ground states in the valence and the conduction band, and the excited state in the valence band.

ramidal shape.[3] One should note, moreover, that the valence band offset between ZnCdSe and ZnSe amounts to only 18% of their bandgap difference, so that the heavy hole confinement in this system should be *almost entirely* determined by the strain. In that respect our system closely resembles InP islands embedded in GaInP, where the unstrained valence band offset is quite small ($\approx$45 meV). This leads us to adopt qualitatively the band profile shown in Ref. 3, where the electron wave function is distributed within the entire island, while the holes are confined to the strain-induced pockets.

This situation is illustrated in Fig. 1, showing a schematic profile of the conduction and valence bands across the dot, in the plane passing through the base of the island. The most important feature of this band profile is the existence of the potential minima (the pockets) around the dot in both the valence and the conduction bands. We will show below that this feature is clearly reflected in the optical properties of the CdSe/ZnSe QD system. As already noted, the existence of such pockets in the conduction band does not have a significant effect on the localization of electrons, because of the combined effects of a large conduction band offset and a light electron mass. In the case of the heavy-hole band, however, such local potential minima can—due to the heavy mass of the holes—result in eigenstates that are sharply localized in the pockets.

The potential profile shown in Fig. 1 then results in two distinct states in the valence band of the QD: a ground state sharply localized in the local potential minima around the dot (denoted as state *B*), and an excited state (denoted as state *A*) confined within the island as a whole. At this point we have to mention that in the case of ZnCdSe dots the strain distribution may be rather asymmetric, due to the random Cd distribution within the dot. We may therefore expect *several* local potential minima with slightly different energies within a given dot, each contributing separately to the optical spectrum. The difference in the degree of localization between states *A* and *B* is, furthermore, expected to have a strong effect on the density of states (DOS) for both these states: the DOS for state *B* can be assumed to be a true delta function due to strong localization within a very small volume (so that it can be treated as zero-dimensional); while the DOS for state *A* is inhomogeneously broadened, since here the wave function is localized within a much larger area (about 20 nm), which is subject to fluctuation in Cd distribution. Note finally that, due to its much smaller DOS, the ground state *B* can be easily saturated, and some heavy holes will then occupy the first excited state even at a low temperature.

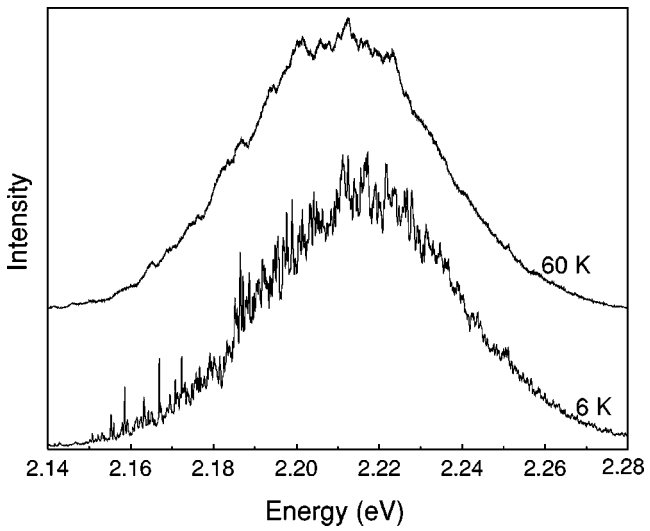

FIG. 2. Micro-PL measurements taken at 6 and 60 K, displaying ultranarrow spikes superimposed on the broad background. Note the disappearance of the sharp structure at 60 K, revealing the existence of much broader structures superimposed on the wide peak.

Based on this picture, two distinct interband transitions are possible: one between the ground state in the conduction band and state *B* (a partially indirect transition, as discussed later); and one between the same conduction band ground state and state *A* in the valence band (a direct transition). It could be argued that the latter transition is forbidden by parity. This is certainly true when one deals with idealized *symmetric* structures. In our case, however, the QD potential may in fact be quite *asymmetric* because of possible irregular shape of the dot, as well as possible fluctuations of composition (and thus also strain). This in turn will result in a relaxation of selection rules,[6] allowing the observation of both transitions simultaneously in optical measurements.

The first piece of experimental evidence indicating that in the case of covered CdSe QDs both types of transitions are observed comes from temperature-dependent micro-PL data. It is already well established by many groups[7–11] that macro-PL experiments on CdSe QDs show very broad lines, typically centered between 2.25 and 2.45 eV, with linewidths of about 60 to 100 meV. Micro-PL experiments resolve these broad spectra into separate emissions from hundreds of individual oscillators, with ultranarrow ($<$0.20 meV) linewidth that reflect the δ function-like density of states of the excitons confined in a box.[7–10] Through the analogy with the InAs/GaAs QD system, it was initially assumed that there is only one state per QD responsible for the PL from these nanostructures, the inhomogeneously broadened macro-PL line being a superposition of the ultranarrow spikes emitted by individual dots.

PL studies as a function of temperature show, however, that the broad macro-PL line persists to above 300 K, while the ultra-narrow spikes observed in micro-PL quench at about 60 K.[10] This behavior is shown in Fig. 2. Detailed temperature studies of micro-PL further showed that the disappearance of the ''spikes'' is not caused by broadening and

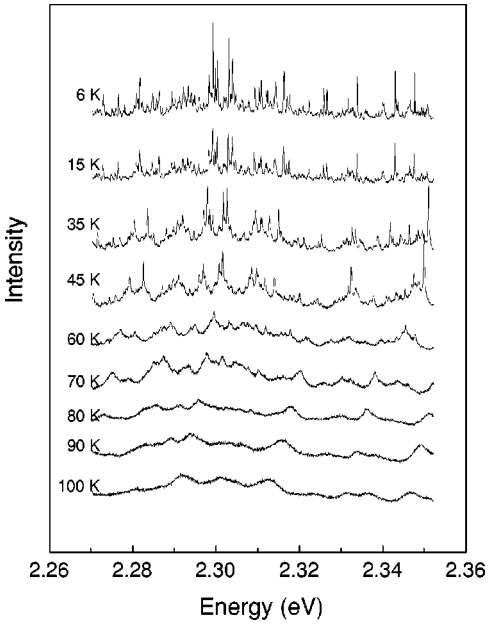

FIG. 3. PL signal from CdSe/ZnSe QDs through a 170 nm aperture taken at several temperatures.

merging into a single wide line.[10] Rather, it is the intensities of the narrow spikes that rapidly decrease, with very little broadening, clearly indicating the disappearance of an oscillator from which they arise. This aspect has been analyzed quantitatively by Kim *et al.*, who show that the narrow PL spikes quench with an activation energy of 4.0 meV, while the broad PL line exhibits an activation energy one order of magnitude larger ($\approx$40 meV).[12]

In order to look more closely into this unexpected behavior, we carried out a series of systematic nano-PL experiments by observing the PL signal from CdSe/ZnSe QDs through a 170 nm aperture. The CdSe QD samples were grown using molecular beam epitaxy, as described elsewhere.[10] The nano-apertures were produced by using 170 nm monodispersed polyspheres as a shadow-mask, on which a thin silver film was deposited. After silver deposition the spheres were washed away, leaving an array of high quality 170 nm apertures. The samples were excited at 438 nm by a doubled-mode-locked Ti-sapphire laser.

Figure 3 shows spectrally resolved nano-PL from an apertured sample taken at several temperatures. The spectrum taken at 6 K exhibits features typical for spectra observed on a selected number of dots, i.e., a large number of ultranarrow spikes. On the other hand, when one looks at the spectrum taken at 100 K, one will note that the spikes have disappeared, but there remain a smaller number of broader lines which appear in the form of an irregular ''modulation'' of the background. Let us now consider the spectra as we lower the temperature from 100 to 6 K. Between 100 and 80 K the spectrum does not change qualitatively, except that the ''modulation'' peaks narrow slightly as the temperature decreases. When we reach 45 K, we observe the coexistence of both features—sharp spikes and broader modulation-like lines—simultaneously. As the temperature is lowered further, the spikes become more intense, overshadowing the broader ''modulation'' lines. The broader lines are, however, still present in the spectrum even at 6K. One should also note the difference in the temperature behavior between the two features. As the temperature increases, the sharp spikes become weaker and broaden slightly. The ''modulation'' peaks, on the other hand, broaden significantly with increasing temperature, and gain in intensity at the expense of the sharp spikes.

We proceed now to the explanation of the observed nano-PL data using the band structure model described earlier. We interpret the two distinct types of transitions (i.e., the sharp spikes prominent at low temperatures, and the broader modulation-like peaks) observed in both micro- and nano-PL, as transitions associated, respectively, with the two states in the heavy hole band (i.e., states *B* and *A* discussed earlier). We believe that the sharp spikes are associated with states *B* localized in the potential minima (the pockets) of the heavy hole band around the dot boundary. The fact that these sharp spikes disappear at 60 K, with only a small activation energy of about 4 meV, indicates that the strain-induced local pockets are not very deep with respect to the overall QD potential, so that carriers in these states can be easily thermalized to the excited state as the temperature increases. We ascribe the broader, modulation-like lines to transitions involving states *A*, which are localized in a much deeper potential well of the quantum dot as a whole, and which therefore persist even to room temperature. This thermalization of holes explains the increasing intensity of the broader lines at the expense of the sharp spikes as the temperature increases.

The above model automatically indicates that the broad line observed in macro-PL is not a superposition of sharp spikes (since they disappear at about 60 K, while the broad line continues to exist well above that temperature), but rather a superposition of transitions involving states *A* that produce the wider, modulation-like lines, which persist to high temperatures (see the nano-PL spectrum for 100 K in Fig. 3).

The difference in the thermal broadening of the two types of lines can be easily explained by considering the DOS of states *A* and *B* (see Fig. 1). The *B* states are truly zero-dimensional states, and thus they should not show thermal broadening. The *A* states on the other hand, are localized within the larger volume of the dot as a whole, and are thus subject to thermal broadening. We note finally that a detailed examination of the data taken in the intermediate temperature region (between 70 and 35 K, where both types of transitions are clearly seen) reveals that *several* narrow spikes occur on top of a single modulation peak. That again indicates that there are several local minima associated with each dot, so that each dot may emit several ultranarrow lines and one broader modulation line.

We will now show that recent time-resolved photoluminescence data observed through a 200 nm aperture on the same samples[13] are also consistent with the model just described. These time-resolved results clearly show that the lifetimes associated with the sharp spikes and with the broad PL spectrum are distinctly different, thus providing further evidence that they involve two distinct types of states. Specifically, excitons associated with the ultra-narrow lines show extraordinarily long lifetimes ($>$4 ns), indicating that in this case the overlap of the electron and the hole wave functions is weak, which suggests that this exciton is spatially indirect. States responsible for the broad emission, on

the other hand, have short lifetimes (approximately 450 ps), indicating that the overlap of electron and hole wave functions is in this case much larger. This feature can be seen by referring to the band diagram sketched in Fig. 1. As already argued, we ascribe the spikes to exciton recombination from the electron ground state, localized primarily in the center of the QD, to the *B* state of the heavy hole, localized in pockets at the edge of the dot. Thus the wave-function overlap between the two carriers is small, making the transition (at least partially) indirect, which will result in a long lifetime. The broad modulation lines, on the other hand, involve states which are both distributed over the entire island (the electron ground state and heavy hole state *A*), so that the resulting transition is characterized by a short exciton lifetime due to the much larger wave-function overlap.

In conclusion, we have shown that a band model predicting the existence of strain-induced pockets in InAs and InP dots accounts for the optical properties observed on the CdSe/ZnSe quantum dots in a consistent manner. The central idea of the model is that the electrons and the first excited state of the valence band, while confined to the QD, are distributed over the entire QD volume; while the heavy hole ground state (owing primarily to the large mass of the heavy hole) is localized in strain-induced pockets at the bottom of the island. This model fully explains our nano-PL data, as well as the recent time-resolved PL results that have already signalled the existence of two different types of excitons in the CdSe/ZnSe system. Thus, although we were not able to perform a quantitative calculation of the band structure due to lack of exact information on the dot topology and composition profile, the model clearly provides a good qualitative understanding of the observed optical properties of CdSe QDs.

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