phys. stat. sol. (c) **1**, No. 4, 779–782 (2004) / **DOI** 10.1002/pssc.200304223

Optical investigation of CdSe/Zn(Be)Se quantum dot structures: size and Cd composition

Y. Gu[*, 1], **Igor L. Kuskovsky**[1], **J. Fung**[1], **G. F. Neumark**[1], **X. Zhou**[2], **S. P. Guo**[2], and **M. C. Tamargo**[2]

[1] Department of Applied Physics and Applied Mathematics, Columbia University, New York, NY 10027, USA
[2] Department of Chemistry, City College of CUNY, New York, NY 10036, USA

Received 22 September 2003, revised 25 September 2003, accepted 20 November 2003
Published online 10 February 2004

PACS 71.35.–y, 78.55.Et, 78.67.Hc

The optical properties of CdSe/$Zn_{0.97}Be_{0.03}Se$ and CdSe/ZnSe quantum dots (QDs) are investigated using photoluminescence (PL) and PL excitation spectroscopies. We show that the addition of Be into the barrier enhances the Cd composition and the overall quantum confinement of optically active QDs. The temperature behavior of PL supports such a conclusion. We also show that the room temperature QD PL exhibits a supra-linear dependence on the excitation intensity, which is attributed to the recombination involving relatively strongly localized holes and quasi-free electrons.

1 Introduction Self-assembled quantum dot (QD) systems have been of great interest due to their unique optical properties, which have promising applications in opto-electronic devices, such as QD laser diodes (LDs). Specifically, III–V semiconductors such as InAs/GaAs and InP/GaP are suitable for LDs in the infrared and red spectral region, and the II–VI system is the material of choice for the green/blue spectral range, in which CdSe/ZnSe is the most studied material so far partly due to its resemblance to the InAs/GaAs system in terms of the bandgap difference and lattice mismatch (~1 eV and ~7%). For the devices applications (especially LDs), QDs with narrow distribution of size and composition are required. However, while with the III–V system the formation of rather uniform QDs can be well controlled by the growth conditions and QDs of sizes below 10 nm with very high packing densities have been obtained (see, e.g. Ref. [1]), it seems to be more difficult to achieve such QDs for the CdSe/ZnSe system.

Recently, beryllium has been introduced into the ZnSe barrier with the expectation to enhance both barrier crystalline quality and QD formation [2, 3]. Moreover, it has been shown [4] that Be helps facilitate island formation in the CdSe/ZnSe system even below critical thickness for Stranski-Krastanow growth. It is thus important to compare the optical properties of CdSe/ZnSe and CdSe/ZnBeSe QD systems. In this paper, we use photoluminescence (PL) and PL excitation (PLE) to investigate both types of QDs.

2 Experimental The CdSe/ZnSe and CdSe/ZnBeSe QD samples investigated in this work were grown under similar conditions with the details of the growth given elsewhere [3]. For PL measurements, samples were excited by the 325 nm emission line from a He–Cd laser. A 300 W Xenon lamp coupled to a 1/4m monochromator was used as an excitation source for PLE experiments. The PL was recorded with a 3/4m monochromator, a thermoelectrically cooled GaAs photomultiplier tube, and a photon counter. The measurements were performed at between 9 K and 293 K, using a closed cycle refrigerator system.

[*] Corresponding author: e-mail: yg99@columbia.edu

3 Results and discussion In Figs. 1(a) and (b) we plot the PLE as well as PL spectra of the CdSe/ZnBeSe and CdSe/ZnSe QD structures, respectively (it must be noted that in both systems there exists intermixing of Cd and Zn in the quantum dots (see, e.g. Ref. [5]); thus, further in the paper, we shall refer to the CdZnSe/ZnBeSe and CdZnSe/ZnSe QDs instead). The PL spectra of both samples are a single relatively broad peak, whose energy depends on the Cd composition (x) and size of the optically active QDs. The PLE spectra for both samples are similar, showing free excitons from the barriers and broad features associated with the excitation via the wetting layers. Interestingly, the PLE spectrum from the CdZnSe/ZnBeSe sample (Fig. 1(a)) also shows a small peak separated from the detection energy (indicated by the arrow) by ~28 meV. A closer look at this region (see the inset) reveals two peaks, which can be fitted well with two Lorentzians. The energy differences between the detection energy and the Lorentzians are 29.0 meV and 21.4 meV. It has been shown by polarized Raman scattering [6] that the former is due to the CdZnSe QD LO phonons, while the latter is due to the QD surface phonons. The absence of such a phonon-assisted excitation in the CdZnSe/ZnSe sample (Fig. 1(b)) suggests a weaker phonon-exciton coupling, and therefore lower Cd composition and/or weaker quantum confinement [7] in this sample.

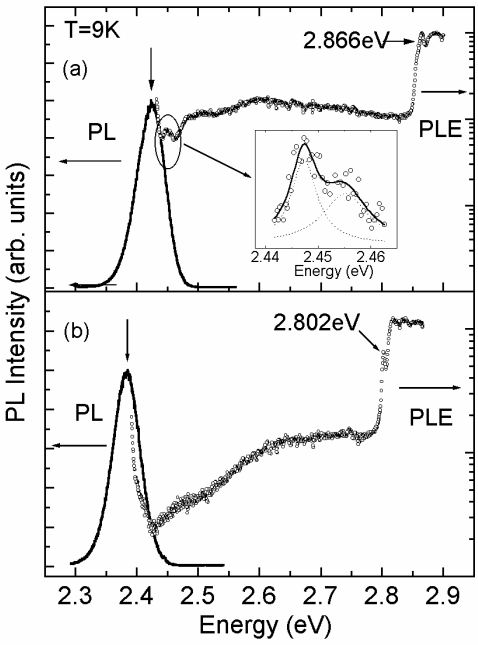

Fig. 1 The PL (solid lines) and PLE (circles) spectra of (a) CdSe/ZnBeSe and (b) CdSe/ZnSe QDs. Arrows indicate the detection energies. The inset is the magnified marked region; the solid line is the fitting result using two Lorentzians (dashed lines).

Using these PL and PLE results combined with the model calculations based on spherical QDs approximation [6, 8], we estimate, for the CdZnSe/ZnBeSe system, the Cd composition (x) in the range of 0.47 to 0.54 and the diameter (d) in the range of 5.1nm to 8.0 nm. A similar procedure [9] assuming a quantum disk model for CdZnSe/ZnSe QDs [8] gives typical x~0.44 and the disk thickness (L_z) of ~2.1 nm. By comparing these results, we suggest that addition of Be into the barrier enhances Cd composition of QDs.

It is important that CdZnSe/ZnBeSe QDs with higher Cd compositions are expected to emit light at the lower photon energies than CdZnSe/ZnSe QDs, since higher Cd composition results in the lower QD bandgap energy. However, the PL of CdZnSe/ZnBeSe QDs is blue-shifted by ~40 meV compared with that of CdZnSe/ZnSe QDs. Since the increase in the barrier bandgap due to the presence of Be cannot account for such a blue shift [10], we suggest that the quantum confinement of optically active QDs in CdZnSe/ZnBeSe is stronger than in CdZnSe/ZnSe. In other words, Be enhances the overall quantum confinement of optically active QDs.

We next discuss the temperature behavior of the PL. The results from CdZnSe/ZnBeSe and CdZnSe/ZnSe samples are shown in Figs. 2 and 3, respectively. The narrowing of the full-width-at-half-maximum (FWHM) of the PL (Figs. 2(a) and 3(a)) within a certain temperature region is typical of a QD-ensemble system (see, e.g. Ref. [11]) and can be attributed to the ionization of QDs with lower activation energies. The red shift of the peak energy compared to the ZnSe bandgap in the same temperature region is consistent with such an explanation. It is interesting that the PL of both sample starts to shift to the blue as the temperature increases further. We attribute this to the ionization of one type of carriers, which will be discussed below in detail.

The PL intensity decreases by four orders of magnitude for the CdZnSe/ZnBeSe sample (Fig. 2(c)), but only by two orders of magnitude for the CdZnSe/ZnSe sample (Fig. 3(c)). Such a discrepancy can be explained by the difference in the overall quantum confinement. As discussed above, the

CdZnSe/ZnBeSe QDs have stronger quantum confinement and thus relatively lower ionization energies, which would result in the lower PL intensity at the higher temperatures.

In Figs. 4(a) and 4(b) we show the integrated PL intensity (I_{PL}) vs. excitation intensity (I_0) in a log–log plot for two temperatures (T = 9 K and T = 293 K) for CdZnSe/ZnBeSe and CdZnSe/ZnSe QDs, respectively. Taking that $I_{PL} \sim I_0^{\alpha}$ we obtain $\alpha \approx 1$ at T = 9 K and $\alpha > 1$ at 293 K. The low temperature behavior is fairly well understood as due to the excitonic recombination. It is interesting that at 293 K $\alpha \approx 2$,

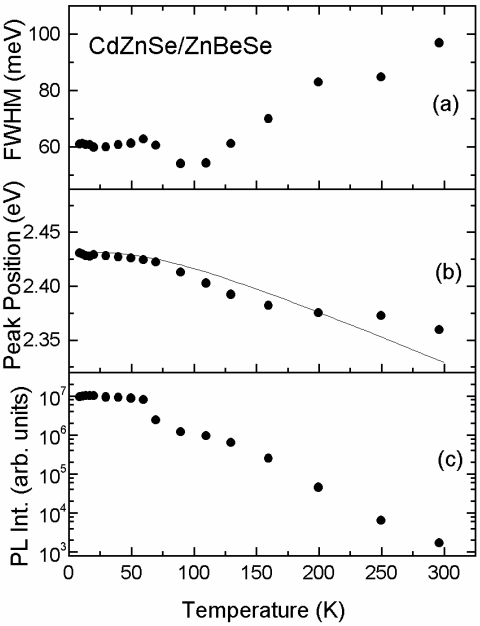

Fig. 2 (a) The FWHM, (b) the PL peak position, (c) the PL intensity of CdSe/ZnBeSe QDs. The ZnSe bandgap (solid line) vs temperature shown is shifted for easier comparison.

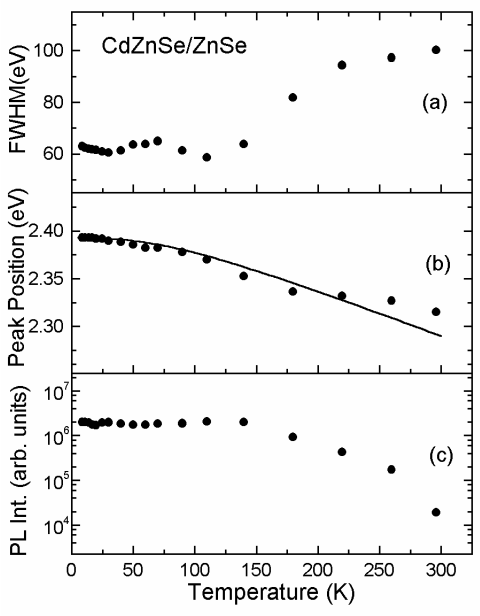

Fig. 3 (a) The FWHM, (b) the PL peak position, (c) the PL intensity of CdSe/ZnSe QDs. The ZnSe bandgap (solid line) vs temperature shown is shifted for easier comparison.

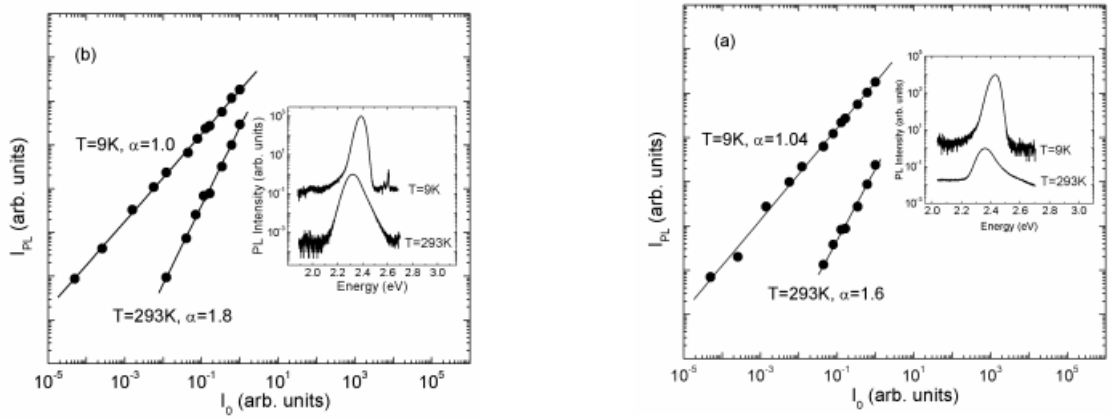

Fig. 4 The log-log plots (solid circles) of the excitation intensity (I_0) dependence of the integrated PL intensity (I_{PL}) of (a) CdZnSe/ZnBeSe QDs and (b) CdZnSe/ZnSe QDs; the solid line are the linear fits. The insets are corresponding PL spectra at T= 9 K and 293 K.

which would be expected for electron-hole recombination. To help with understanding of this phenomenon, we plot in the insets the PL spectra at the same temperatures. It is clear that at T = 293 K both PL spectra show a tail on the high energy side, which is not observed at T = 9 K. Such a tail indicates recombinations involving extended states. The PL peak's blue shift mentioned above for T > 200 K supports our contention that at high temperatures the extended states participate in the recombination. For instance, assuming that the electrons are relatively weakly localized in the QDs, the PL transition at T=293K could be due to recombination between the holes localized in the QDs and the quasi-free electrons, resembling a free-to-bound (FB) transition. In fact, FB PL is characterized by a long tail on the high energy side (see, e.g. Ref. [12] and references therein). Since in our case $\alpha < 2$, it is likely that portion of the PL band is still due to excitonic recombination. We note that similar observations of supralinear behavior have been reported in Ref. [13] for InAs/GaAs QDs, where it has been attributed to the independent escape and capture of electrons and holes.

3 Summary In summary, we have investigated optical properties of CdSe/ZnBeSe and CdSe/ZnSe QDs using PL and PLE spectroscopies. We have shown that, the addition of Be into the barrier enhances the Cd composition and the overall quantum confinement of optically active QDs, and thus the LO phonon-exciton coupling in such QDs. The PL temperature behavior of these two samples has also been investigated and is consistent with our conclusions. Additionally, the room temperature PL studies have shown that at relatively high temperatures the emission is mostly due to radiative recombination between strongly localized holes and quasi-free electrons, resembling a FB transition.

Acknowledgement This work is supported in part by New York Science and Technology on Photonic Materials and Applications and Center for Analysis of Structures and Interfaces in CUNY (X.Z, S.P.G and M.C.T)

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