Determination of size and composition of optically active CdZnSe/ZnBeSe quantum dots

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The size and composition of optically active $Cd_xZn_{1-x}Se/Zn_{0.97}Be_{0.03}Se$ quantum dots (QDs) are determined using photoluminescence, photoluminescence excitation, and Raman scattering spectroscopies combined with a model of photoluminescence and LO phonon energies. The diameters of optically active QDs range from 5.1 to 8.0 nm with Cd composition in the range of 47%–54%, corresponding to the "small" QDs group. Additionally, surface phonons from QDs are observed in this system. © *2003 American Institute of Physics.*
[DOI: 10.1063/1.1623941]

Self-assembled quantum dot (QD) systems have been of great interest due to their unique optical properties, which have promising applications in optoelectronic devices, such as QD laser diodes. Specifically, II–VI semiconductors are the materials of choice for the green/blue spectral range. The most studied II–VI system is CdSe/ZnSe QDs (which are in fact CdZnSe QDs due to Cd/Zn interdiffusion).

From previous transmission electron microscopy (TEM) studies,[1–3] it has been shown that there are two types of QDs coexisting in molecular beam epitaxy-grown $Cd_xZn_{1-x}Se/ZnSe$ nanostructures: (1) "small" QDs with diameters (d) smaller than 10 nm and Cd composition (x) of ~ 0.1–0.6, and (2) "large" QDs with d about 20 nm and $x \sim 0.5$–0.7. For device applications, it is crucial to correlate TEM observations with optical studies to determine properties (x and d) of optically active QDs. This has been attempted by studying photoluminescence (PL) of samples that are also characterized by TEM (see, e.g., Ref. 3). However, to obtain the specific x and d of QDs that contribute to the PL, a more careful analysis is required.

In this work, we show how to use PL, PL excitation (PLE), and Raman spectroscopies, complemented by simple model calculations, to estimate x and d of optically active QDs using CdZnSe/ZnBeSe with ~ 2.5 ML of CdSe deposition[4] as an example. We use ZnBeSe rather than the conventional ZnSe as a barrier material, as Be has been recently introduced into the ZnSe barrier with the expectation to enhance both barrier crystalline qualities and QD formation.[4,5]

To estimate x and d of the QDs that are responsible for such PL, we first calculate the PL transition energy as a function of these two parameters. The results (dashed lines) are plotted in Fig. 1(a) together with low temperature ($T = 9$ K) PL (solid line) with 325 nm excitation. The calculation is based on the following assumptions: (1) The QDs are considered to be spherical;[6] (2) only the ground state of QDs is considered, since only a single PL peak is observed even at

the highest excitation intensity (~ 28 W/cm^2) and the integrated PL intensity as a function of excitation intensity shows a single slope (not shown); (3) the shifts of the band edges due to the hydrostatic component of strain are calculated independently;[7,8] (4) the QDs are considered free of Be, since the Be concentration is low even in the barrier; (5) for the barrier ($Zn_{0.97}Be_{0.03}Se$) properties, the ZnSe values are used except for the band gap energy (E_G), which is calculated using the relation given in Ref. 9; and (6) the material
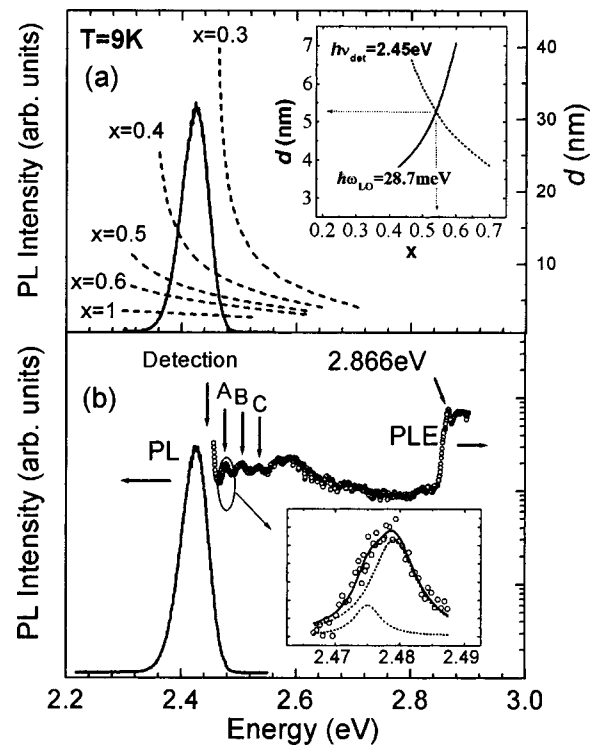

FIG. 1. (a) The calculated PL emission energies (dashed lines) for $Cd_xZn_{1-x}Se/Zn_{0.97}Be_{0.03}Se$ QDs as a function of x and d. The PL spectrum is also shown for excitation at 325 nm. The inset shows the procedure for estimation of x and d of QDs emitting at $h\nu_{det}$. (b) The PLE (open circles, semilog scale) for the $Cd_xZn_{1-x}Se/Zn_{0.97}Be_{0.03}Se$ QD sample. Arrows indicate the detection energy and three equally spaced peaks. The inset is the magnification of the marked region with the solid line being the result of the fitting with two Lorentzians (dashed lines).

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TABLE I. Parameters for CdSe and ZnSe.

Parameters[a]	CdSe	Ref.	ZnSe	Ref.
E_G (eV) at $T=10$ K	1.75	12	2.82	13
C_{11} (10^{10} N/m^2)	6.67	14	8.26	7
C_{12} (10^{10} N/m^2)	4.63	14	4.98	7
$0.5a_c \approx a_v \approx a_G$[b] (eV)	−3.45	14	−5.82	7
m_{hh}/m_0	0.45	14	0.78	15
m_e/m_0	0.11	14	0.15	15
b (eV)	−0.8	14	−1.2	7,14
Lattice constant (Å)	6.052	14	5.668	14
$\hbar\omega_{LO}$ (meV)	25.8	17	31.4	13
β_{LO}[c] (m/s)	5000	18		
$d\omega/dp$[c] (cm^{-1}/GPa)	5.0	16		

[a]See Ref. 10.
[b]See Ref. 11.
[c]For simplicity, we use the CdSe value for Cd$_x$Zn$_{1-x}$Se QDs.

parameters for Cd$_x$Zn$_{1-x}$Se are obtained by linear interpolation between those of pure CdSe and ZnSe (see Table I) except for E_G, where a quadratic dependence on x is used with the bowing parameter $B=0.35$.[14]

In Fig. 1(b) we plot the PLE spectrum of CdZnSe/Zn$_{0.97}$Be$_{0.03}$Se QDs ($T=9$ K) taken at the detection energy ($h\nu_{det}$) of 2.45 eV (indicated by the arrow), along with the PL. The PLE spectrum consists of a sharp strong peak at ~2.866 eV, which corresponds to the free exciton energy in Zn$_{0.97}$Be$_{0.03}$Se,[9] a rather broad feature below this peak, which is presumably due to excitation via the CdZnSe wetting layer (WL), and three equally spaced peaks (indicated by A, B, and C) adjacent to the detection energy. The last three peaks are consistently observed at various $h\nu_{det}>2.43$ eV (not shown here), below which only one peak (peak A) can be observed. The energy separation between these three peaks and the difference between the detection energy and peak A is ~28 meV, which is in the range of the CdZnSe LO phonon energy ($\hbar\omega_{LO}$) (see Table I). Furthermore, the intensities of these three peaks decrease with decreasing $h\nu_{det}$ for reasons to be discussed later. A more careful investigation [see the inset of Fig. 1(b)] of peak A reveals that it can be fitted well with two Lorentzians, separated from $h\nu_{det}$ by ~28.7 meV (peak 1) and 24.7 meV (peak 2), respectively. Such a procedure has been carried out at several detection energies across the PL peak, and the results are summarized in Table II. While peak 1 (~28.7–29.3 meV) can be understood as due to the LO phonon from Cd$_x$Zn$_{1-x}$Se QDs with a given x, peak 2 (~24.7–21.4 meV) is below the bulk energy values of CdSe LO phonon[19] and thus is likely due to a different origin.

To further understand the origins of these peaks, polar-

TABLE II. Estimated Cd composition (x) and diameter (d) of CdSe/ZnBeSe QDs and corresponding LO phonon and surface phonon energies.

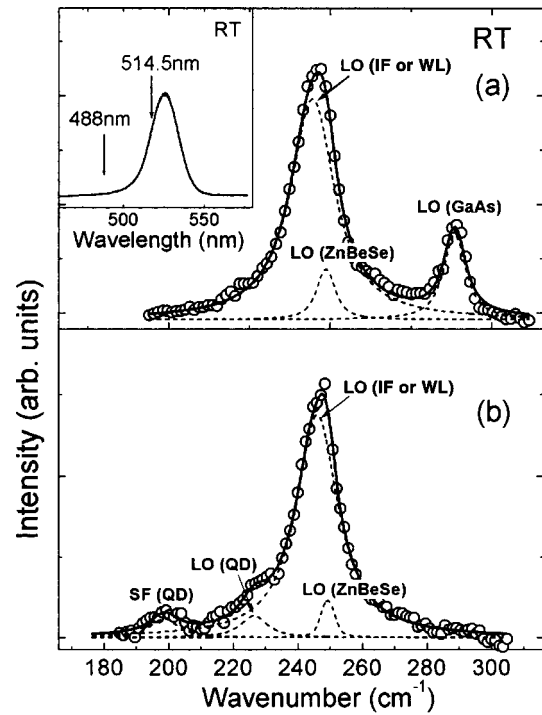| $h\nu_{det}$ (eV)	Peak 1 (LO) (meV)	Peak 2 (SF) (meV)	x	d (nm)
2.470	28.7	24.7	0.53	5.1
2.450	28.7	24.7	0.54	5.3
2.441	28.7	22.4	0.54	5.4
2.431	28.8	21.8	0.53	5.7
2.426	29.0	21.4	0.51	6.4
2.422	29.3	22.0	0.47	8.0
2.417	29.2	22.0	0.49	7.4

FIG. 2. The RT polarized Raman scattering spectra for Cd$_x$Zn$_{1-x}$Se/Zn$_{0.97}$Be$_{0.03}$Se QDs: (a) using the nonresonant 488 nm line of an Ar$^+$ laser and (b) using the 514.5 nm line, which is resonant with the QD RT PL (see the inset) with excitation at 325 nm. Open circles are the experimental data, and the solid line is the result of fitting with Lorentzians (dashed lines).

ized Raman scattering spectroscopy was performed in the configuration with only LO phonon scattering is allowed. In Figs. 2(a) and 2(b) we plot Raman spectra taken at the room temperature on the CdZnSe/Zn$_{0.97}$Be$_{0.03}$Se QDs, with the 488 and 514.5 nm lines of an Ar$^+$ laser, respectively. When excited with the 488 nm line, which is in the region where there is only very weak PL emission (see the inset), the Raman spectrum shows two main peaks: one is a symmetric peak at ~289 cm^{-1} (35.8 meV), which we attribute to GaAs LO phonons;[20] the other has an asymmetric lineshape and can be fitted with two Lorentzians peaked at ~249 cm^{-1} (30.9 meV) and ~244 cm^{-1} (30.3 meV). We attribute the 249 cm^{-1} peak to Zn$_{0.97}$Be$_{0.03}$Se LO phonons, whose energy is expected to be the same as the ZnSe LO phonon energy (253 cm^{-1})[13] due to the low Be content; note that this value is lower, which is explained by tensile strain, since Zn$_{0.97}$Be$_{0.03}$Se has a slightly smaller lattice constant than GaAs. The 244 cm^{-1} peak could be attributed either to the interface (IF) phonons between the CdZnSe/ZnBeSe layers,[21] or to the LO phonons in the WL with ~30% Cd.

The Raman spectrum using the 514.5 nm line, where this laser line is resonant with the PL emission, shows additional features vis-a-vis the nonresonant (488 nm) spectrum. First, a low energy shoulder on the main peak at ~226.8 cm^{-1} (28.1 meV) is seen; this is very close to the energy of peak 1 observed in PLE. Therefore, considering its energy and that it appears only under the resonant condition, we attribute it to LO phonons in the CdZnSe QDs. Second, an additional small peak at ~198.6 cm^{-1} (24.6 meV) appears; it corresponds to peak 2 observed in PLE. Since it also appears only in resonant Raman scattering, it seems likely that this peak

has its origin in the QDs too. Peak 2 and the 198.6 cm^{-1} peak are between the CdSe LO and TO phonon energies; similar peaks have been previously observed for CdSe QDs embedded in glass[22,23] and have been attributed to surface (SF) phonons of QDs. Similar features have also been observed in PLE studies of CdZnSe/ZnSe nanostructures,[24,25] but no clear identification was given. At this time we attribute this peak to CdZnSe QD SF phonons.

We now quantitatively estimate $\hbar\omega_{LO}(x,d)$ for CdZnSe QDs as a function of x (including strain) and d. First, assuming the linear interpolation between CdSe and ZnSe LO phonon energy values (see Table I) and using the pressure dependence of $\hbar\omega_{LO}$, we calculate $\hbar\omega_{LO}$ as a function of x. Then, we obtain $\hbar\omega_{LO}(x,d)$, using the theory developed in Refs. 26 and 27 that shows that LO phonon energies decrease with decreasing QD size. The parameters used for this calculation are summarized in Table I.

Having obtained $\hbar\omega_{LO}(x,d)$, we are now able to estimate x and d of the QDs emitting at a given wavelength. From PLE, we obtain $\hbar\omega_{LO}(x,d)$, which is the phonon energy of QDs emitting at a specific energy, $h\nu_{det}$. $h\nu_{det}$ can also be expressed in terms of x and d (see the PL calculation earlier). Thus, the intersection of the "d vs x" plots for a $\hbar\omega_{LO}(x,d)$ and the corresponding $h\nu_{det}(x,d)$ gives the unique combination of the QD size and Cd composition that satisfies both conditions simultaneously. In the inset of Fig. 1(a), we show such a procedure for QDs emitting at $h\nu_{det}=2.45$ eV (dashed line) with $\hbar\omega_{LO}(x,d)=28.7$ meV (solid line); this gives $x=0.54$ and $d=5.3$ nm. Applying this method to several points on the PL curve we obtain (Table II) that 5.1 nm $<d<8$ nm and $0.47<x<0.54$, which corresponds to the small QDs group.[1] The radii of QDs (2.5–4.0 nm) are smaller than the exciton Bohr radius in CdSe ($\sim$5.4 nm),[28] suggesting strong quantum confinement.

The decrease of the phonon peaks from PLE with decreasing $h\nu_{det}$ is attributed to the dependence of phonon-excition coupling strength on Cd composition and QD size,[29] where the strength decreases with increasing dot size above some critical radius. Also, the SF phonon energy (peak 2) generally decreases with increasing QD size (Table II). This was predicted in Ref. 30 and observed in Raman scattering studies of CdSe QDs embedded in glass.[23] Therefore, our estimation of QD d and attribution of this peak to SF phonons are consistent with each other.

In summary, we have shown how to model the PL and LO phonon energies from PL, PLE, and Raman scattering spectroscopies in order to estimate the Cd composition and size of optically active $Cd_xZn_{1-x}Se/Zn_{0.97}Be_{0.03}Se$ QDs as an example. The results show that the QDs in these structures belong to the small QD group observed from TEM.

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