Size-dependent strain effects in self-assembled CdSe quantum dots with $Zn_{0.38}Cd_{0.23}Mg_{0.39}Se$ barriers

J. S. Reparaz,[a] A. R. Goñi, and M. I. Alonso
Institut de Ciència de Materials de Barcelona-CSIC, Esfera UAB, 08193 Bellaterra, Spain

M. N. Perez-Paz and M. C. Tamargo
Department of Chemistry, City College of The City University of New York, New York, New York 10031

From resonant Raman scattering measurements under hydrostatic pressure the authors were able to identify both the strain-shifted longitudinal optical phonon of CdSe quantum dots with different average size embedded in a quaternary ZnCdMgSe material and a Mg-local dot mode due to interdiffusion from the barrier. They show that the large tunability of the light emission, which covers most of the visible spectrum, is not only due to a different degree of confinement but also to a size-dependent built-in strain. The frequency of the Mg mode allowed them also to roughly estimate the amount of Mg interdiffusion into the quantum dots. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2402881]

Strain-driven low-dimensional heterostructures of group II-VI semiconductors have been extensively studied because of their potential applications in optoelectronics. In particular, quantum dot (QD) structures are expected to lead to improvement in the performance of light emitting diodes and semiconductor lasers.[1] Important advances in the fabrication of these zero-dimensional structures have been obtained using different methods.[2,3] The CdSe/ZnCdMgSe system, for instance, is particularly attractive due to its intense photoluminescence (PL) even at room temperature and the wide energy range it offers to tune the QD emission. Recently, great progress has been achieved in the degree of control and reproducibility of the growth process by introducing Mg into the barrier material.[4] In this way, dots with unimodal size distributions are obtained, in which the average dot size and hence the emission energy of the CdSe QDs can be easily adjusted by varying the CdSe deposition time. Furthermore, the large gap-energy difference of 1 eV between CdSe and the quaternary barrier material allows for the tuning of the QD PL throughout the visible spectrum from the red to the blue.

In this letter we show how we made explicit use of the resonant enhancement of the Raman scattering signal to identify vibrational modes stemming from CdSe/ZnCdMgSe QDs of different sizes, from which we were able to determine the built-in strain and degree of Mg interdiffusion into the dots. Different laser lines were brought into resonance with the fundamental optical transition of the CdSe dots by applying high hydrostatic pressures up to 6 GPa. An important result concerns the observation of size-dependent strain effects from which follows that the band-gap tunability of the CdSe/ZnCdMgSe dot system is due to a non-negligible part of at least 18% to the reduction of the built-in strain with decreasing average dot size.

The CdSe/ZnCdMgSe samples were grown by molecular beam epitaxy on InP (001) substrates. First a 150 nm thick lattice-matched InGaAs buffer layer was deposited followed by a Zn exposure for later reduction of the defect density in the ZnCdMgSe barrier. A 6 nm ZnCdSe layer is used to promote the two-dimensional nucleation after which 400 nm of $Zn_{0.38}Cd_{0.23}Mg_{0.39}Se$ was grown as barrier material. Finally, pure CdSe is deposited for dot growth in the Stranski-Krastanow mode followed by another 130 nm barrier of $Zn_{0.38}Cd_{0.23}Mg_{0.39}Se$. A 6 nm ZnCdSe cap layer was used to prevent the oxidation of the barrier material. The average base radius of the QDs is about 47 nm, whereas their height is ranging between 3 and 15 nm depending on the CdSe deposition time. The QD density is about 7×10^8 cm^{-2}. Here we present data from two samples with deposited thicknesses of 3.6 and 5.9 ML of CdSe and room temperature emission peaking at 2.23 and 2.03 eV, respectively. More details of the sample growth and their structural characterization are given elsewhere.[4]

Resonant Raman measurements were performed in backscattering geometry using two different laser lines for excitation, 514.5 and 632.5 nm. Spectra were acquired with a LabRam HR800 micro-Raman system. In order to meet resonance conditions in the different samples we applied high hydrostatic pressures using the standard diamond anvil cell (DAC) technique. Spectra under pressure were measured with crossed linear polarization to suppress the reflected laser beam from the DAC. A 4:1 mixture of methanol and ethanol was employed as pressure-transmitting medium. Pressure was monitored *in situ* by the shift of the ruby R1 line.[5] The samples loaded in the DAC were previously chemically etched to a thickness of about 1 μm. An etchant solution of 3:2 HCl to H_3PO_4 was used to selectively etch away the InP substrate.

Figure 1 shows Raman scattering spectra of samples A and B with nominally 3.6 and 5.9 ML of CdSe, respectively, measured at ambient temperature and pressure conditions using the red (1.96 eV) and green (2.41 eV) laser lines for excitation. Up to four peaks are apparent in Raman spectra, from which the one at around 220 cm^{-1} and the broader peak centered slightly above 300 cm^{-1} are identified as the longitudinal-optical (LO) phonon of the CdSe dots and a Mg local mode also from the QDs, respectively. This assignment is based on the fact that the LO CdSe mode is only observed under near resonance conditions of the laser with the fundamental PL emission from the dots, which is attained with the
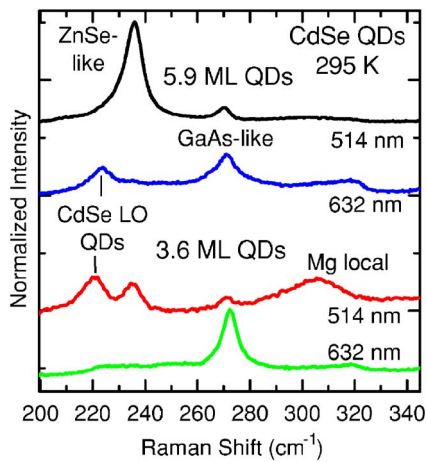
a)Electronic mail: sebareparaz@hotmail.com

FIG. 1. (Color online) Polarized Raman spectra at ambient pressure and temperature conditions of samples A and B with nominally 3.6 and 5.9 ML of CdSe, respectively, using the red (632.5 nm) and green (514.5 nm) laser lines for excitation.
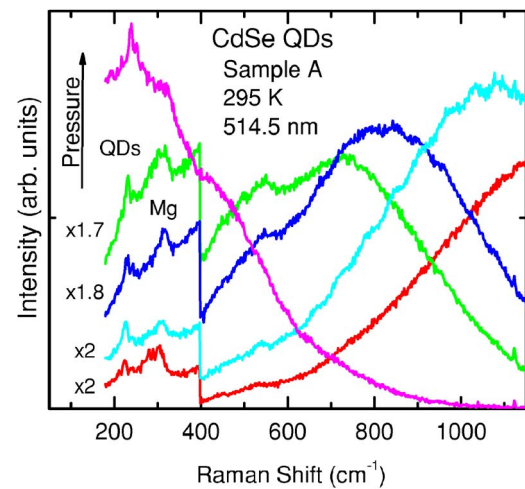

FIG. 2. (Color online) Evolution of the luminescence and resonant Raman peaks with hydrostatic pressure for sample A using the 514.5 nm laser line for excitation. The five spectra correspond to the pressure values: 0.8, 1.0, 1.8, 2.1, and 3.4 GPa.

green line for sample A and with the red line for sample B, as illustrated in Fig. 1. The 300 cm^{-1} Mg-local mode is also observed together with the 220 cm^{-1} peak for 514.5 nm excitation laser line, which suggests that Mg from the barrier is present inside the QDs. Although this peak is not observed when exciting with the red laser line, pressure measurements support this hypothesis. In contrast, both modes are absent in the Raman spectra of a control sample without CdSe dots but containing the barrier material, independently of the laser wavelength used for excitation. The peak at 235 cm^{-1}, which clearly resonates with green excitation in both samples, is attributed to the ZnSe-like LO mode of the 6 nm thick ZnCdSe cap layer, whereas the nonresonant Raman peak at 272 cm^{-1} corresponds to the GaAs-like LO phonon of the InGaAs buffer layer. We point out that the Raman selection rules measured with linearly polarized light at ambient pressure conditions are consistent with the previous assignment of the peaks.

In order to fully settle the issue of the identification of QD Raman modes, we have fine-tuned the fundamental PL emission of sample A to the energy of the 514 nm laser line by applying high hydrostatic pressure up to 6 GPa. In Fig. 2 we display several Raman spectra measured at small pressure steps in the range from 0.8 to 3.4 GPa. The broad band, which in this representation of the spectra as a function of relative wave numbers, shifts with increasing pressure towards the laser line corresponds to the PL emission from the CdSe dots. This is due to the strong increase with pressure of the energy of the fundamental optical transition of the dots with a slope of about 47 meV/GPa.[6] The only Raman peaks which resonate with the PL emission from the CdSe dots are the two ones previously assigned to the LO CdSe mode at around 220 cm^{-1} and the Mg-local mode near 300 cm^{-1}. Their Raman intensity is not only comparable to that of the dot PL but it also increases as these modes become more in outgoing resonance with the PL band, as the applied pressure increases. Interestingly, we observe a third Raman peak at around 520 cm^{-1} at low pressure, which is also in outgoing resonance with the CdSe QD emission (see Fig. 2). We believe that this Raman peak corresponds to exciton-mediated multiphonon scattering by a combination of the LO CdSe

and the Mg-local mode due to strong electron-LO-phonon coupling in the highly polar II-VI compounds.[7]

Valuable information about the strain status of the CdSe dots is obtained from a quantitative analysis of the frequency and its pressure dependence of the QD vibrational modes. In Fig. 3 we have plotted for sample A the peak position of both QD phonon modes as a function of the applied pressure. The solid lines represent the result of least-squares fits to the data points using linear functions yielding

$$\omega_{\text{LO-CdSe}} = 219(1)\ \text{cm}^{-1} + 5.4(3)\ \frac{\text{cm}^{-1}}{\text{GPa}} \times P, \qquad (1)$$

$$\omega_{\text{Mg-local}} = 301(2)\ \text{cm}^{-1} + 7.5(8)\ \frac{\text{cm}^{-1}}{\text{GPa}} \times P, \qquad (2)$$

where P is the external hydrostatic pressure in GPa. The large difference in the pressure slopes is only apparent and almost vanishes after normalization by the mode frequency to calculate the mode Grüneisen parameter according to $\gamma_i = -(B_0/\omega_i(0))(\delta\omega_i/\delta P)$, where $B_0 = 53$ GPa is the bulk
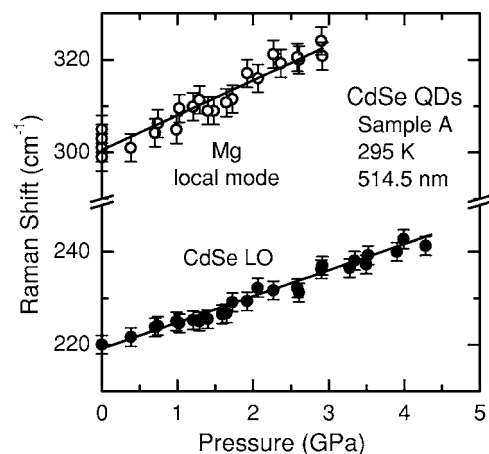

FIG. 3. Pressure dependence of the mode frequencies in sample A for the LO CdSe and Mg-local modes. The different values quoted at zero pressure for the Mg-local mode correspond to spectra measured outside the DAC with the four possible configurations of the linear polarization of incident and scattered beams.

modulus of CdSe (Ref. 8) and $\omega_i(0)$ is the mode frequency in cm^{-1} at zero pressure. For the LO CdSe and the Mg-local mode of the dots we obtain $\gamma = 1.30 \pm 0.08$ and $\gamma = 1.32 \pm 0.12$, respectively. The peak position of the broad band corresponding to the Mg-local mode at ambient pressure ranges from 300 to 305 cm^{-1} depending on the linear polarization configuration (see Fig. 3). The lower frequencies are obtained with crossed polarization, as for the Raman measurements under pressure, explaining why extrapolated value from the fit to the pressure data points at $P=0$ is at 301 cm^{-1}.

Both the frequency of the Mg-local mode at zero pressure and the coincidence of its Grüneisen parameter with that of the LO phonon indicate a low degree of Mg interdiffusion from the quaternary barrier into the nominally pure CdSe dots. Using a modified linear diatomic-chain model for the calculation of the Mg local-mode frequency in a zinc blende CdSe and ZnSe host[9] and by comparing with the only available data for $Zn_{1-x}Mg_xSe$ alloys,[10] the zero-pressure frequency of 305 cm^{-1} measured with parallel polarization at ambient pressure gives an upper bound for the Mg concentration in the QDs in the 1% range.

Returning to the LO mode of the CdSe QDs, its zero-pressure value of 219 cm^{-1} for sample A appears to be blueshifted by 14 cm^{-1} from the bulk value of 205 cm^{-1}.[11] This is due to the large built-in strain in the quantum dots.[12] Using the pressure coefficient of Eq. (1) we infer that the LO phonon of the dots senses an average compressive stress of about 2.6 GPa.[13] This huge internal pressure has an impact on the electronic as well as optical properties of the CdSe QDs. For instance, using the measured pressure coefficient for the PL dot emission of about 47 meV/GPa (Ref. 6) it turns out that the energy of the fundamental optical transition contains a strain-induced blueshift of approximately 120 meV.

A striking result is obtained by comparing the ambient pressure values of the LO phonon of the dots for sample A (219 cm^{-1}) and sample B (223 cm^{-1}). The small difference of 4 cm^{-1}, which is systematic and beyond experimental uncertainty, indicates that the built-in compressive stress in sample B is about 0.75 GPa larger than in sample A. This gives clear evidence that bigger dots are subjected to larger average internal stresses, as predicted by valence-force field calculations of the strain distribution in lattice mismatched dot structures.[14] These results indicate that the hydrostatic (main) component of the average built-in strain varies from $\approx \Delta\epsilon$, the lattice mismatch, for the case of very flat quantum dots with aspect ratios (base length over dot height) over 10 up to a value as high as $3\Delta\epsilon$ for large size dots for which the aspect ratio tends to unity. This reflects the change in strain status from a biaxially strained thin layer to a three-dimensional situation, where the dot is strained in all directions. Again, the 0.75 GPa stress difference between the larger QDs of sample B as compared with the smaller ones

of sample A translates into an energy shift of 35 meV for the fundamental dot emission. Although this is only 18% of the actual energy difference of 200 meV between the PL peaks in both samples, which is mainly given by quantum confinement, it is now obvious that size-dependent strain effects cannot be neglected at all for an accurate tuning of the QD optical emission.

In summary, we have applied high hydrostatic pressure to samples of self-assembled CdSe quantum dots with ZnCd-MgSe barriers in order to identify the vibrational modes of the dots by the resonant enhancement of their Raman intensity. This technique allowed us to detect a small amount of interdiffused Mg from the barriers and, what is more important, to probe the internal strain status of the dots. An interesting observation concerns the fact that the built-in strain of the CdSe QDs scales with their average size, an effect which ought to be considered along with quantum confinement for any quantitative analysis of the electronic, optical, and vibrational properties of this low-dimensional semiconductor system.

[1] *Nano-Optoelectronics*, edited by M. Grundmann (Springer, Berlin, 2002).
[2] C. B. Murray, D. J. Norris, and M. G. Bawendi, J. Am. Chem. Soc. **115**, 8706 (1993).
[3] T. Tawara, S. Tanaka, H. Kumano, and I. Suemune, Appl. Phys. Lett. **75**, 235 (1999).
[4] M. N. Perez-Paz, X. C. Zhou, M. Munoz, H. Lu, M. Sohel, M. C. Tamargo, F. Jean-Mary, and D. L. Akins, Appl. Phys. Lett. **85**, 6395 (2004).
[5] H. K. Mao, J. Xu, and P. M. Bell, J. Geophys. Res. **91**, 4673 (1986).
[6] J. S. Reparaz, A. R. Goñi, M. I. Alonso, M. N. Perez-Paz, and M. C. Tamargo, Phys. Status Solidi B (to be published).
[7] R. M. Martin and C. M. Varma, Phys. Rev. Lett. **26**, 1241 (1971); A. García-Cristobal, A. Cantarero, C. Trallero-Giner, and M. Cardona, Phys. Rev. B **49**, 13430 (1994).
[8] M. L. Cohen, Phys. Rev. B **32**, 7988 (1985).
[9] G. Lucovsky, M. H. Brodsky, and E. Burstein, Phys. Rev. B **2**, 3295 (1970).
[10] D. M. Huang, C. X. Jin, D. H. Wang, X. H. Liu, J. Wang, and X. Wang, Appl. Phys. Lett. **67**, 3611 (1995).
[11] A. P. Alivisatos, T. D. Harris, L. E. Brus, and A. Jayaraman, J. Chem. Phys. **89**, 5979 (1988).
[12] H. Rho, H. E. Jackson, S. Lee, M. Dobrowolska, and J. K. Furdyna, Phys. Rev. B **61**, 15641 (2000).
[13] Strain profiles calculated within different self-consistent elasticity theories indicate that the average hydrostatic strain in the central region of a quantum dot, as probed by Raman scattering, is in good approximation homogeneous. See, for example, C. Pryor, J. Kim, L. W. Wang, A. J. Williamson, and A. Zunger, J. Appl. Phys. **83**, 2548 (1998).
[14] C. Kristukat, Ph.D. thesis Technische Universität Berlin, Berlin, 2006; http://opus. kobv. de/tuberlin/volltexte/2006/1237/pdf/kristukat_christian. pdf.