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Exciton–Phonon Scattering in CdSe/ZnSe Quantum Dots *

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A temperature-dependent photoluminescence measurement is performed in CdSe/ZnSe quantum dots with a ZnCdSe quantum well. We deduce the temperature dependence of the exciton linewidth and peak energy of the zero-dimensional exciton in the quantum dots and two-dimensional exciton in the CdSe wetting layer. The experimental data reveal a reduction of homogeneous broadening of the exciton line in the quantum dots in comparison with that in the two-dimensional wetting layer, which indicates the decrease of exciton and optical phonon coupling in the CdSe quantum dots.

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Excitonic effects in semiconductor quantum wells (QWs) and quantum dots (QDs) have been studied extensively aiming at both fundamental and technologically important properties.[1−4] For the polar semiconductor, the asymmetry bond structure and large gradient of atom potential give rise to a strong scattering of excitons with phonons, and the interaction of excitons and phonons dominantly controls the linewidth and energy shift of the excitonic emission peak in these semiconductor systems.[4−8] QWs and QDs preserve bulk crystal structure. However, excitonic behaviour in low dimensional structures, such as QDs, is significantly different from those in bulk materials due to localization of exciton and quantum confinement. It was generally reported that the exciton longitudinal optical (LO) phonon coupling in QWs shows a drastic reduction with the enhancement of dimensional confinement.[6−8] Whilst in one-dimensional GaAs/AlAs quantum wires, exciton–LO phonon scattering is enhanced by over 35% compared to a QWs,[9] as resulted from the additional space confinement.

The lifetime of the zero-dimensional excitons (ZDEs) in the CdSe QDs is significantly enhanced compared to the ZnCdSe/ZnSe QW due to the three-dimensional confinement in real space.[10] On the other hand, CdSe QDs have a strong electron–hole exchange interaction.[11] This implies that the scattering of ZDEs and phonons in CdSe QDs can be restrained to some extent. For high-quality QDs, an excitonic device can be expected even at room temperature. However, due to the small exciton Bohr radius of CdSe (∼3 nm), the quantum effect cannot evidently be observed in CdSe QDs. Self-assembled CdSe QDs on the ZnSe base layer originating from the Stranski–Krastanow (SK) growth mode can give emissions from both CdSe QDs and the CdSe wetting layer (similarly one quasi-QW inserted between the ZnSe base layer and CdSe QDs).[12] Therefore, we can gain a deep insight into the interaction of phonons and excitons in QDs by photoluminescence (PL) spectroscopy. In this Letter, we report on the temperature dependence of PL spectra of CdSe/ZnSe QDs. The exciton linewidth increase and peak energy shift are discussed on the basis of exciton and phonon scattering.

The sample under investigation has been grown on a GaAs(110) surface by molecular beam epitaxy. QDs were formed by a three monolayer (ML) CdSe wetting layer (WL) deposited on a 1 μm thick ZnSe buffer layer. Atomic force microscopy showed that dots in the sample exhibited a right circle cone with an average height of 5 nm, a base diameter of about 10 nm and ten dots per μm^2. A 20 nm ZnSe barrier layer, a 7 nm $Zn_{0.72}Cd_{0.28}Se$ QW and a 50 nm ZnSe cladding layer were successively capped on the CdSe QDs. The critical thickness of CdSe active layer for QD formation is 3 ML, where transition from two-dimensional (2D) to three-dimensional growth mode, i.e. the SK mode, takes place.[10,12] The GaAs substrate was etched off by wet etching. The details of the sample growth and wet etching process are described elsewhere.[13]

Figure 1 shows the PL spectra of the sample at 60 K. The spectra were measured using the third harmonic of the 1.064 μm line of a 10 Hz pulse YAG laser with a power less than 1 mW and a pulse duration of 6 ns as an excitation source, and detected by a spex monochrometer with a photomultiplier tube. The sample was mounted on a copper pole in a continuous helium flow cryostat, and its temperature adjusted from 10K to 250 K. At 60 K, the sample revealed a broad and intense emission at 2.08 eV with an unresolved shoulder at the high-energy side, and two weak peaks at 2.41 and 2.54 eV. According to Ref. [12], the broad and intense emission at about 2.08 eV originates from excitons in the CdSe QDs and the PL emission with peak at about 2.4 eV is attributed to the excitons in the CdSe wetting layer. In our previous work,[14,15] the comparative sharp peak at 2.54 eV is confirmed from the ZnCdSe QW. However, we are interested in the evolution of emission from the CdSe QDs and the

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wetting layer with temperature. Figure 2 shows the PL spectra of the CdSe QDs and CdSe wetting layer in the temperature range of $10 - 250$ K. It is noticed that, when the temperature increases, the redshift and broadening of the intense peak can be observed significantly, and the shoulder located at about 2.15 eV shifts slightly and becomes obvious. The shoulder peak is considered to come from a certain localized state, since it exists up to room temperature. Simultaneously the weak peak near 2.4 eV also shows redshift and expands. It is expected that the enhancement of interaction of excitons and phonons with temperature leads to the redshift and broadening of exciton emission.

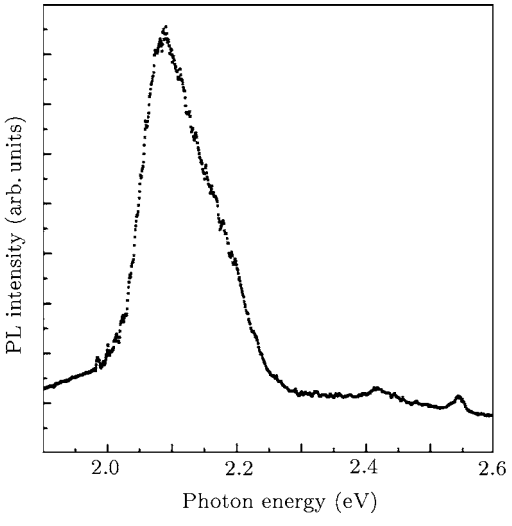

Fig. 1. PL spectrum of CdSe WL/CdSe QDs/ZnSe/ZnCdSe QW at 60 K.

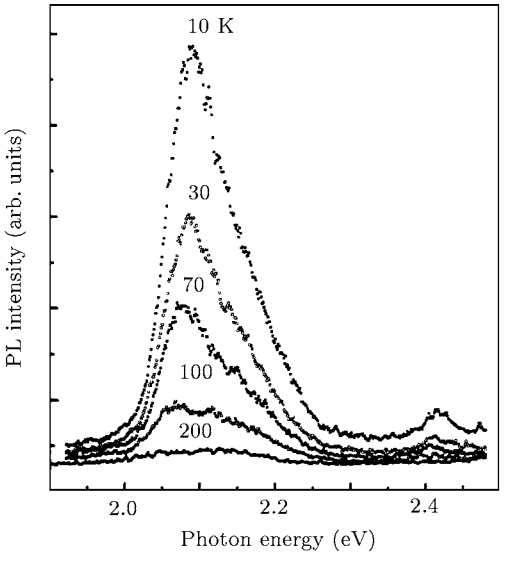

Fig. 2. PL spectra corresponding to CdSe QDs and CdSe wetting layer in CdSe WL/CdSe QDs/ZnSe/ZnCdSe QW at various temperatures.

We analysed the lineshape of the exciton emission peaks of the wetting layer and CdSe QDs. It is known that the line broadening in general is composed of inhomogeneous and homogeneous terms. The inhomogeneous broadening ($\Gamma_{\rm inh}$) is due to the fluctuations of circumstance such as size or composition, which is independent of temperature. The homogeneous term ($\Gamma_{\rm h}$) is mainly caused by the exciton and phonon interaction. In general, polar semiconductors undergo a much stronger Fröhlich interaction (interaction of excitons with LO phonons) than deformation potential interaction (interaction with acoustic phonons). The exciton line broadening is predominantly determined by inhomogeneous broadening at low temperature, which can be obtained from Gaussian function fitting of PL spectra. The homogeneous term can be obtained at higher temperatures by fitting the exciton line with a complex Voigt function. Here, in order to simplify the calculation, we fit the emission peak with a Gaussian function for all temperatures. To fit exciton emission in the QDs, the attribution of the shoulder peak is also included for a satisfactory fit of the spectra.

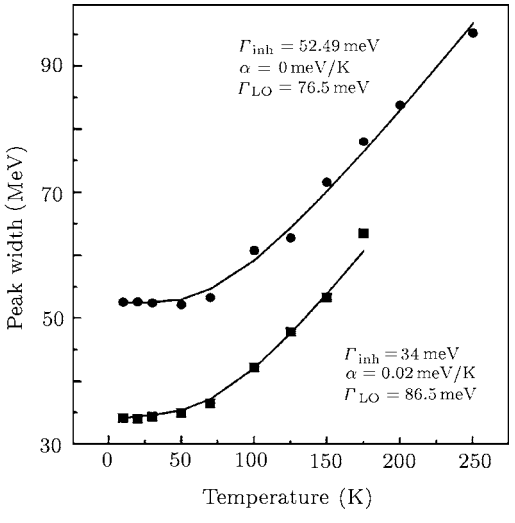

Fig. 3. Linewidth of PL peak dependence on temperature in the range of $10 - 250$ K. The upper corresponds to the peak at about 2.10 eV, and the lower to the peak at about 2.4 eV. The circles and squares show the experimental data, and the lines represent the fitting by Eq. (1).

Figure 3 shows the temperature dependence of the linewidth (Γ) deduced for excitons in the CdSe QDs and wetting layer from the PL spectra. We can clearly see that Γ increases gradually with temperatures up to 70 K, but increases rapidly above 70 K. The temperature dependence of the linewidth can be expressed by the Bose–Einstein statistical factor for Fröhlich interaction and a linear term in T for the deformation potential. It is known that $\Gamma(T)$ at low excitation intensity can be described as the following simple expression[5]

$$\Gamma(T) = \Gamma_{\rm inh} + \alpha T + \Gamma_{\rm LO} \left[\exp\left(\hbar\omega_{\rm LO}/k_{\rm B}T\right) - 1\right]^{-1}, \quad (1)$$

where α is the coefficient of exciton–acoustic-phonon scattering. $\Gamma_{\rm LO}$ represents the exciton–LO-phonon

coupling strength; $\Gamma_{\rm inh}$, $\Gamma_{\rm LO}$ and α can be determined experimentally from measurements of temperature dependence of Γ; $\hbar\omega_{\rm LO}$ is the LO-phonon energy. Here we use the LO-phonon energy (25.4 meV) of the bulk CdSe to substitute that of the wetting layer. However, the dot size and strain dependence of the LO-phonon frequency causes a high-energy shift of the phonon in the CdSe QDs.[16,17] Atomic force microscopy showed that dots in the sample have an average height of 5 nm. Referring to the literature,[16,17] we estimate $\hbar\omega_{\rm LO} = 27$ meV for the CdSe QDs. Comparing the data of Fig. 3 with Eq. (1), we obtain the parameters in Eq. (1). For the QDs, $\Gamma_{\rm inh} = 52.5$ meV, $\Gamma_{\rm LO} = (76.5 \pm 3)$ meV, and $\alpha = 0$ meV/K. For the wetting layer, $\Gamma_{\rm inh} = 34$ meV, $\Gamma_{\rm LO} = (86.5 \pm 4)$ meV, and $\alpha = 0.02$ meV/K. Because QDs have a distribution of dot size and a partial alloying with ZnSe at the interface,[18,19] the energy level separation the between initial and final states of electron transition is different for individual dots due to the quantum confinement effect and strain potential. The contribution of individual dots causes the large inhomogeneous broadening. The value of $\Gamma_{\rm inh}$ determined here for the CdSe QDs is 50% more than that of the wetting layer, implying that the dot size fluctuation significantly influences the line broadening.

Within the lower temperature range, the temperature dependence of the linewidth is determined by the second term of Eq. (1). For QDs, the second term does not exhibit a distinct dependence on temperature, while for the wetting layer it slightly shows a temperature dependence. The term presents the exciton–acoustic-phonon interaction, and α is dependent on the dimensionality of the system and on the deformation potentials of the conduction and valence bands. In the present case, the measurement result within the data error limit hinting at the quasi-zero-dimensional QDs can diminish the exciton and acoustic-phonon scattering. The $\Gamma_{\rm LO}$ value of the QDs decreases by more than 10% compared to that for the wetting layer. In a polar semiconductor, the contribution of the exciton–LO phonon scattering to exciton linewidth is mainly due to the transition from an initial exciton state (at $K \approx 0$) to a free electron–hole pair state by absorption of the LO-phonon via the Fröhlich interaction. The rate of these transitions is dominantly determined by the matrix element of the Fröhlich Hamiltonian for exciton–LO phonon interaction and the LO-phonon Bose occupancy factor at a certain temperature.[20] In the polar system, the electron is more delocalized than the hole in an exciton, and the charge distribution asymmetry forms the exciton polarity. The charge inhomogeneity couples to the polar lattice via the Fröhlich interaction. The confinement of the size can compress the extent of the wavefunction of the exciton and can induce an enhancement of the exciton binding energy.[6] The compression of exciton will make it less polar, and thus decrease the coupling of excitons to LO phonons.[21] The difference between $\Gamma_{\rm LO}$ in QDs and in the wetting layer is likely to be mainly due to the difference in exciton polarity in quasi-zero and two dimensions.

The phonon coupling of excitons simultaneously induces the PL emission energy shift of the exciton line for QDs and the wetting layer with temperature. At temperatures lower than 60 K, the PL peaks hardly shift. The exciton emission energy decreases almost linearly with temperature when T is higher than 70 K.

In conclusion, we have investigated the temperature dependence photoluminescence of CdSe QDs and the wetting layer and found a reduction of exciton–phonon coupling in the QDs compared with the 2D wetting layer.

References

[1] Schmitt-Rink S, Chemla D S and Miller D A B 1989 *Adv. Phys.* **38** 89

[2] Yamaguchi S, Kurusu H, Kawakami Y and Fujita S 2000 *Phys. Rev.* B **61** 10 303

[3] Humlicek J, Schmidt E, Bocanek L, Svehla R and Ploog K 1993 *Phys. Rev.* B **48** 5241

[4] Wan J Z, Brebner J L, Leonelli R, Zhao G and Graham J T 1993 *Phys. Rev.* B **48** 5197

[5] Lee J, Koteles E S and Vassell M O 1986 *Phys. Rev.* B **33** 5512

[6] Pelekanos N T, Ding J, Hagerott M, Nurmikko A, Luo H, Samarth N and Furdyna J 1992 *Phys. Rev.* B **45** 6037

[7] Fujimoto M, Shigematsu H, Semda K, Yoshikawa M, Kubo H, Yamada Y and Taguchi T 1999 *Japan. J. Appl. Phys.* **38** 3550

[8] Ramvall P, Tanaka S, Nomura S and Riblet P 1999 *Appl. Phys. Lett.* **75** 1935

[9] Gopal A V, Kumar R, Vengurlekar A V, Melin T, Laruelle F and Etienne B 1999 *Appl. Phys. Lett.* **74** 2474

[10] Kummell T, Weigand R, Bacher G, Forchel A, Leonardi K, Hommel D and Selke H 1998 *Appl. Phys. Lett.* **73** 3105

[11] Kulakovskii V D, Bacher G, Weigand R, Kummell T, Forchel A, Borovitskaya E, Leonardi K and Hommel D 1999 *Phys. Rev. Lett.* **82** 1780

[12] Ko H, Park D, Kawakami Y, Fujita S and Fujita S 1997 *Appl. Phys. Lett.* **70** 3278

[13] Zhang L, Kong X, Shen D and Fan X *J. Appl. Phys.* (submitted)

[14] Yu G, Fan X W, Zhang J Y, Zheng Z H, Yang B J, Zhao X, Shen D Z and Kong X G 1999 *J. Phys. D: Appl. Phys.* **32** 1506

[15] Yu G, Fan X, Zhang J, Yang B, Shen D and Zhao W 1998 *J. Electron Mater.* **27** 1007

[16] Rho H, Robinson L M, Smith L M, Jackson H E, Lee S, Dobrowolska M and Furdyan J K 2000 *Appl. Phys. Lett.* **77** 1813

[17] Rho H, Jackson H E, Lee S, Dobrowolska M and Furdyan J K 2000 *Phys. Rev.* B **61** 15 641

[18] Lowisch M, Rabe M, Kreller F and Henneberger F 1999 *Appl. Phys. Lett.* **74** 2489

[19] Gindele F, Woggon U, Langbein W, Hvam J, Leonardi, Hommel D and Selke H 1999 *Phys. Rev.* B **60** 8773

[20] Nomura S and Kobayashi T 1992 *Phys. Rev.* B **45** 1035

[21] Alivisatos A P, Harris T S, Carroll P J, Steigerwald M I and Brus I E 1989 *Chem. Phys. J.* **90** 3463