Spectroscopy of the Forming Process of Quantum Dots Accompanied by the Thinning of Wetting Layer

2005 Chinese Phys. Lett. 22 708

(http://iopscience.iop.org/0256-307X/22/3/052)

Spectroscopy of the Forming Process of Quantum Dots Accompanied by the Thinning of Wetting Layer *

ZHANG Zhen-Zhong(张振中)**, SHEN De-Zhen(申德振), ZHANG Ji-Ying(张吉英), SHAN Chong-Xin(单崇新), LIU Yi-Chun(刘益春), LU You-Ming(吕有明), FAN Xi-Wu(范希武)

Key Laboratory of Excited State Processes, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Sciences, Changchun 130033

(Received 19 September 2004)

A series of $Cd_{0.44}Zn_{0.56}Se/ZnSe$ sandwich structures with different $Cd_{0.44}Zn_{0.56}Se$ embedded layer thicknesses were fabricated by metal organic chemical vapor deposition. When the embedded layer thickness exceeded 3.0 nm, the photoluminescence spectra of the sample changed into the two-band structure from the one-band structure, and atomic force microscopy images indicate that $Cd_{0.44}Zn_{0.56}Se$ quantum dots were formed. In the two-band photoluminescence spectrum, the band at the low energy side was attributed to be from quantum dots, and the high-energy one arose from the wetting layer. Thinning of the wetting layer with quantum dots forming was confirmed indirectly by the significant blue shift of the wetting-layer photoluminescence band compared to the photoluminescence band of the samples for which the $Cd_{0.44}Zn_{0.56}Se$ layer thickness was less than 3.0 nm. This thinning arose from mass migration during the Stranski–Krastanow growth of $Cd_{0.44}Zn_{0.56}Se$ quantum dots.

PACS: 78.55.Et, 78.67.De, 78.67.Hc

Quantum dots (QDs) have attracted great interest recently due to the significance in basic research and potential application.[1−3] The studies on the growth processes of QDs including the forming and ripening were important branches of all the research on QD systems, but the improvements were mostly obtained on large-mismatching systems, such as InAs/GaAs and CdSe/ZnSe. Most of these works were carried out by using transmission electron microscopy, reflection high-energy electron diffraction, atomic force microscopy, and so on.[4−7] Photoluminescence (PL) studies of quantum structures with different embedded layer thicknesses have also been reported.[8−11] As reported in the literature, there are two-dimensional (2D) PL peaks showing monotonic red shifts when quantum dots are formed with increasing deposition thickness. However, in CdSe/ZnSe systems, the large lattice mismatch (6.8%) will lead to the result that the critical thickness of CdSe layer on ZnSe is too small (about 0.9 nm). In CdSe/ZnSe quantum structures with different CdSe thickness, the thickness fluctuation of the CdSe layer has a great influence on the PL measurement result because the mean thickness of the CdSe layer is not large enough in comparison with its thickness fluctuation. In addition, with the increasing CdSe deposition thickness, the transformation from 2D-growth to 3D-growth seems too "fast" for studying in detail. In this Letter, we take $Cd_xZn_{1-x}Se$ as the embedded layer in place of CdSe. The Zn content in the $Cd_xZn_{1-x}Se$ is 0.56. The lattice mismatch between $Cd_{0.44}Zn_{0.56}Se$ and ZnSe is decreased to 3% and the calculated critical thickness is increased to 3.1 nm.[12] Because the critical thickness is enlarged, the forming process of $Cd_{0.44}Zn_{0.56}Se$ quantum dots is "slowed down" significantly. With the $Cd_{0.44}Zn_{0.56}Se$ QDs forming, a blue shift of 2D-like luminescence from the wetting layer is observed in the PL spectra.

All the samples were grown on GaAs (100) substrates by metal organic chemical vapour deposition. The growth temperature is 310°C. Dimethyl cadmium, dimethyl zinc and H_2Se were used as precursors. Total pressure was kept at 3200 Pa. Before growth, the substrates were annealed at 600°C for 10 min. The growth rates for $Cd_{0.44}Zn_{0.56}Se$ and ZnSe were 0.06 and 0.07 nms^{-1}, respectively. The $Cd_{0.44}Zn_{0.56}Se$ layer thicknesses were 1.8, 2.1, 2.5, 3.0 and 3.6 nm for different samples, which were estimated according to growth time. After each $Cd_{0.44}Zn_{0.56}Se$ layer was deposited, there is a 60-s interruption. All the samples consist of 5 periods separated by 15 nm of ZnSe barriers and were protected with 60 nm of ZnSe caplayers. A Jobin-Yvon 630 micro-spectrograph was employed to measure the photoluminescence of the samples. An Ar-ion laser was operated at 488 nm as the excitation source.

The room-temperature PL spectra of the samples with different $Cd_{0.44}Zn_{0.56}Se$ layer thicknesses are shown in Fig. 1. For convenient comparison, the PL intensities of the samples with the $Cd_{0.44}Zn_{0.56}Se$ layer thicknesses 2.5, 3.0 and 3.6 nm are magnified

* Supported by the National High Technology Development Programme of China under Grant No 2001AA311120, the Key Project of the National Natural Science Foundation of China under Grant No 60336020, the Knowledge Innovation Project of Chinese Academy of Sciences, the National Natural Science Foundation of China under Grant Nos 60278031, 60176003, and 60376009.

** Email: zhang_z_z@hotmail.com

to appropriate scales. Due to the continual weakening of quantum confinement, the PL band shifts from 2.38 eV to 2.31 eV with increasing $Cd_{0.44}Zn_{0.56}Se$ layer thickness to 2.5 nm. When the thickness reaches 3.0 nm, the PL spectrum with one-band structure changes into two bands. One shifts to low energy (band A) and the other appears at 2.39 eV (band B), which is higher than the emission energy of the former three samples. When the $Cd_{0.44}Zn_{0.56}Se$ layer thickness is increased to 3.6 nm, band A shows a red shift of 16 meV, and the intensity of band A decreases by 40%. Band B shifts to low-energy side by 45 meV.

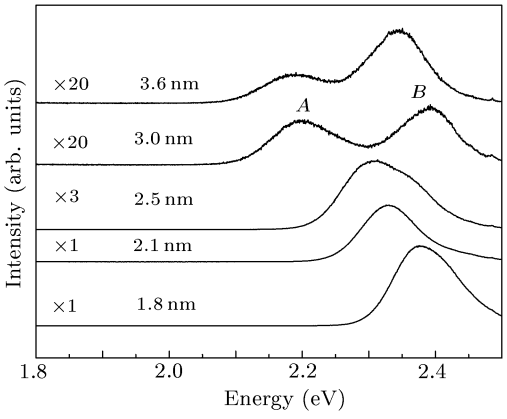

Fig. 1. Room-temperature PL spectra of the samples in thicknesses 1.8, 2.1, 2.5, 3.0 and 3.6 nm of the $Cd_{0.44}Zn_{0.56}Se$ layer.

In our previous work,[12] it was reported that the fabrication of $Cd_{0.44}Zn_{0.56}Se$ QDs with Stranski–Krastanow mode, where the calculated critical thickness of $Cd_{0.44}Zn_{0.56}Se$ on ZnSe is near 3.1 nm and the forming of high-density QDs was observed by using atomic force microscopy (AFM) when the $Cd_{0.44}Zn_{0.56}Se$ layer approached the calculated critical thickness, which means that the appearance of the two PL bands in Fig. 1 is related to the formation of the QDs. In order to study the origin of the two emission bands, PL spectra at various temperatures of the sample with 3.0 nm $Cd_{0.44}Zn_{0.56}Se$ embedded layer were shown in Fig. 2(a). The intensities of all the spectra were normalized to 1. Figure 2(b) depicts the temperature dependence of full width at half maximum (FWHM) of bands A and B. For band A, the FWHM varies in a small scale as the temperature increases in the range from 80.2 K to 167.4 K, which suggests that band A is originated from $Cd_{0.44}Zn_{0.56}Se$ QDs due to the delta function density of state of QDs.[13] According to Ref. [10], we attributed band B to the luminescence of the wetting layer. Band B shows a significant widening with increasing temperature till 197.4 K. However, in the range from 197.4 K to 242.4 K, there appears a dramatic decrease of the FWHM of band B.

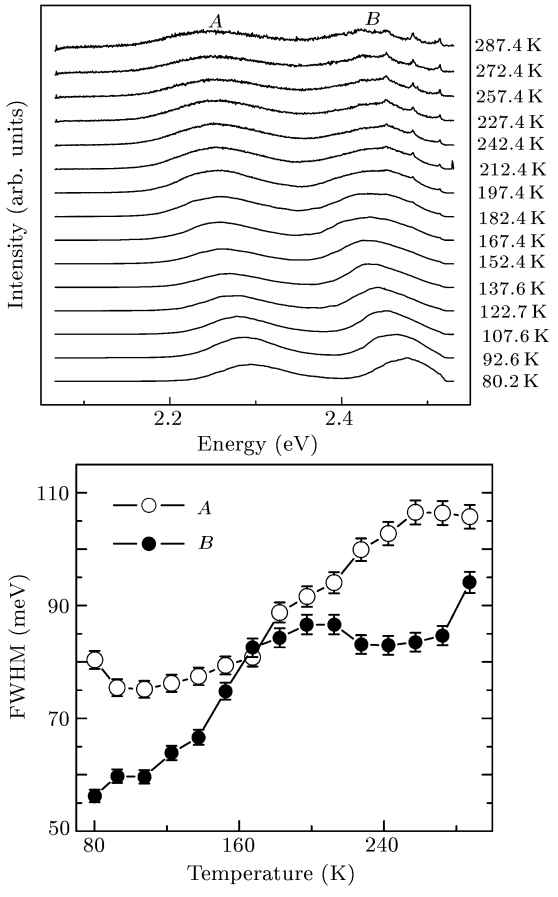

Fig. 2. (a) The PL spectra evolution of the sample with the 3.0-nm $Cd_{0.44}Zn_{0.56}Se$ embedded layer with increasing measure temperature. (b) Temperature dependences of the FWHM of band A (open circles) and band B (closed circles).

In Fig. 1, the energy of band B is higher than that of the samples with a thinner $Cd_{0.44}Zn_{0.56}Se$ embedded layer (even to 1.8 nm). Based on the quantum confinement effect, it can be concluded that the wetting layer thickness is smaller than 1.8 nm. In the growth process of QDs with the Stranski–Krastanow mode, strain relaxation plays an important role for forming QDs.[14] When the $Cd_{0.44}Zn_{0.56}Se$ thickness is beyond the critical value, the system will decreases the strain energy by forming QDs. Some atoms transfer onto the dots from the adjacent areas to reduce the system energy.[15] For the sample with the 3.0-nm $Cd_{0.44}Zn_{0.56}Se$ layer, the bottom diameter of the QDs can reach about 85 nm and the surface density is 8×10^9 cm^{-2}.[12] Both the values are larger than those reported in the literature.[16–18] Forming so large and dense QDs will expend a mass of $Cd_{0.44}Zn_{0.56}Se$, which brings about a significant thinning of the wetting layer. Considering that the PL energy of band B is higher than that of the sample with the 1.8-nm embedded layer, the forming and ripening of the QDs expend no less than 1.2 nm thickness of $Cd_{0.44}Zn_{0.56}Se$.

When the $Cd_{0.44}Zn_{0.56}Se$ layer thickness increases to 3.6 nm, band A, which comes from the QDs, shows a red shift of 16 meV, and the intensity decreases by 40%. This suggests that the size of the dots increases and the density decreases. The PL of the wetting layer shifts to low-energy-side by 45 meV, which indicates that the wetting layer is thicker than that of the sample with 3.0 nm of $Cd_{0.44}Zn_{0.56}Se$.

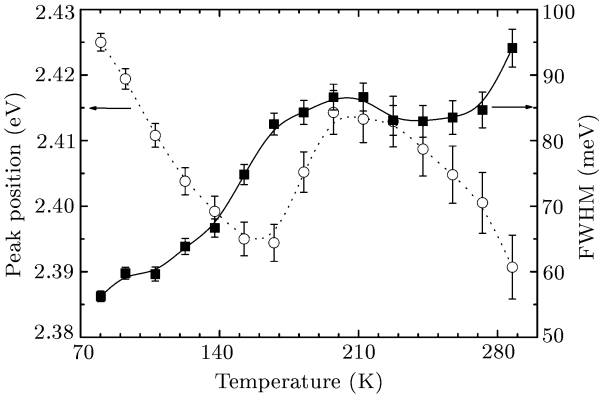

Fig. 3. Temperature dependences of the peak position and the FWHM for band B.

In order to study the anomalous decrease of the FWHM of band B appeared in the range from 197.4 K to 242.4 K in Fig. 2(b), we depict the variation of position of band B in Fig. 3 together with the temperature dependence of the FWHM. An anomalous blue shift of band B between 167.4 K and 197.4 K can be observed. The anomalous temperature dependences of band position and FWHM indicate that band B is not a simple peak but a superposition of more than one emission peaks from excitons at adjacent localized states. The unconventional evolvements of band B are originated from the redistribution of excitons between these levels as increasing temperature.[19] In low temperature range, with increasing temperature, band B shifts to lower-energy side due to the decrease of the band gap. Further increase of temperature activates excitons from lower-energy levels to higher-energy ones, which causes lower-energy emissions to decrease and higher-energy emission to be enhanced. Therefore, band B shifts to the high-energy side. When lower-energy emissions can be ignored, band B begins to show normal red shift. The gradual attenuation of lower-energy emission peaks also results in the decrease of the FWHM of band B in the range from 197.4 K to 242.4 K. Because of the influence of band A on the fitting of band B, it is difficult to give the energy difference between these localized states precisely. The two-Gauss-peak fitting on band B shows that the energy difference is about 25 meV. This result excludes the possibilities as follows: (1) energy difference between the first and second quantum levels, which should be larger than 25 meV by far because the energy difference between the first and second quantum levels of the heavy hole has already reached 30 meV; (2) energy difference between the first heavy-hole and the first light-hole quantum levels, which is 60 meV; (3) energy difference between free exciton and donor bound exciton level, which often fluctuates near 5 meV in CdZnSe.[19] Therefore, the energy difference in this Letter should originate from the thickness fluctuation of the wetting layer or Cd composition fluctuation in the wetting layer. Because of limitation of the characterization condition, further analysis on the origin of energy difference will be discussed elsewhere.

In summary, $Cd_{0.44}Zn_{0.56}Se/ZnSe$ quantum structures with different $Cd_{0.44}Zn_{.056}Se$ layer thicknesses have been fabricated and the PL characteristics of the samples have been investigated. The PL spectra of the QDs and the wetting layers have been observed when the $Cd_{0.44}Zn_{0.56}Se$ layer thickness reaches a critical thickness. The blue shift of wetting layer PL band originates from the surface mass transfer. The anomalous temperature dependence of the PL band of the wetting layer is caused by the redistribution of excitons between localized states. According to the calculation in the report of Ko *et al.*, the formation of the localized state levels can be attributed to the thickness fluctuation of the wetting layer or Cd composition fluctuation in the wetting layer.

References

[1] Rho H et al 2000 *Appl. Phys. Lett.* **77** 1813
[2] Litvinov D et al 2001 *J. Appl. Phys.* **89** 3695
[3] Krestnikov I L et al 1999 *Phys. Rev.* B **60** 8965
[4] Schikora D et al 2000 *J. Cryst. Growth* **214/215** 698
[5] Suemune I et al 1997 *Appl. Phys. Lett.* **71** 3886
[6] Ohishi M et al 2000 *J. Cryst. Growth* **214/215** 690
[7] Yang Z et al 2003 *Chin. Phys. Lett.* **20** 2001
[8] Matsumura N, Saito T and Saraie J 2001 *J. Cryst. Growth* **227/228** 1121
[9] Straβburg M et al 2000 *J. Cryst. Growth* **214/215** 756
[10] Kim C S et al 2001 *J. Cryst. Growth* **214/215** 761
[11] Leon R et al 2000 *Appl. Phys. Lett.* **76** 2074
[12] Shan C X et al 2002 *J. Vac. Sci. Technol.* B **20** 1102
[13] Matsumura N et al 2000 *J. Cryst. Growth* **214/215** 694
[14] Eaglesham D J and Cerullo M 1990 *Phys. Rev. Lett.* **64** 1943
[15] Yang Y et al 2001 *J. Cryst. Growth* **233** 785
[16] Xin S H et al 1996 *Appl. Phys. Lett.* **69** 3884
[17] Leonardi K et al 1997 *Appl. Phys. Lett.* **71** 1510
[18] Kurtz E et al 1998 *J. Cryst. Growth* **184/185** 242
[19] Ko H C et al 1998 *Appl. Phys. Lett.* **73** 1388