

Growth and optical characteristics of ZnCdSe/ZnSe QWs on Si substrate with ZnO buffer

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In this paper, the growth and characteristics of ZnCdSe/ZnSe quantum wells (QWs) prepared on ZnO-Si (111) templates are reported. An oriented ZnO thin film with a smooth surface was employed to be the buffer layer for the ZnCdSe/ZnSe QWs growth. Scanning electron microscopy (SEM) patterns showed that the ZnO buffer layer improved the smoothness of the ZnCdSe/ZnSe sample. Up to the 3rd longitudinal optical phonon of Zn_{0.56}Cd_{0.44}Se observed in Raman spectra suggests that the crystal quality of ZnCdSe/ZnSe QWs is reasonably good. The influence of quantum confinement effect on exciton characters of the QWs was also demonstrated.

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Wide band gap II-VI heterostructures containing quantum wells (QWs) are of major scientific and technological interest, in particular, ZnCdSe/ZnSe QWs have attracted much attention as continuous wave (CW) blue-green light emitting devices^[1,2]. The growth of ZnCdSe/ZnSe QWs in combination with Si material is particularly appealing, which promises a method of integrating high-quality wide-band-gap optoelectronic devices, such as electroluminescent (EL) devices^[3], light emitting diodes (LED)^[4], and so on, with mature micro-electronic technique. However, the direct growth of II-VI materials on Si is an arduous task because of their large difference in the chemical and mechanical properties. Further more, the poor wetting of the polar compounds on nonpolar silicon substrates impedes the direct nucleation and consequently results in poor quality and morphology of the epilayer. Adding a zinc oxide (ZnO) buffer layer between the epilayer and Si substrate can be a promising way to overcome the abovementioned difficulties. In the present work, the growth of Zn_{0.56}Cd_{0.44}Se/ZnSe QWs on ZnO coated Si substrate was carried out, and samples with higher quality than those grown on bare Si substrate were obtained. The effect of quantum confinement on excitonic and Raman characters of the QW structures is investigated.

Semi-insulating Si (111) wafers were employed as the substrates. The Si substrates were cleaned according to the procedure detailed in Ref. [5], which begins with a degreasing step followed by wet chemical etching. Then the substrates were passivated with a thin oxide layer, and finally, the oxide layer was removed by dipping the wafers into hydrofluoric acid. After the cleaning procedure, the substrates were loaded into the growth chamber of a plasma enhanced chemical vapor deposition (PECVD) equipment to deposit a ZnO buffer layer^[6]. The silicon wafers coated with ZnO layer were placed into the growth chamber of LP-MOVPE equipment. Firstly,

168-nm-thick ZnSe buffer layers were grown on the Si substrate, and then 5 periods of ZnCdSe/ZnSe QWs, the barrier layer is 14 nm thick and the well widths are 1.4, 1.7, 1.9, 2.1 and 2.4 nm for five samples respectively. The top of the QWs was coated with a 42-nm-thick ZnSe cap layer. Intentional growth interruption for about 60 seconds between ZnSe and ZnCdSe layers was adopted to obtain abrupt interface. The growth temperature was maintained at 310 °C throughout the growth, with the pressure fixed at 3×10^4 Pa. Dimethylzinc, dimethylcadmium and hydrogen selenide were used as precursors.

Photoluminescence (PL) and Raman measurements were carried out using an Ar⁺ laser (488 nm) as the excitation source, and a charge-coupled device (CCD) of a JY-630 micro-Raman spectrograph designed specially for wide gap semiconductors.

Typical scanning electrical microscopic (SEM) micrographs of the ZnCdSe/ZnSe QWs grown on Si (111) substrate with (sample A) and without a ZnO buffer layer (sample B) are shown in Figs. 1(a) and (b), respectively. In each case the surfaces of the QWs exhibit a mosaic structure. However, the surface of sample B is more spotty than that of sample A. Furthermore, there are microcracks on the surface of B.

We believe the microcracks are due to the stress that originates from the large difference in thermal expansion coefficients between the epilayer and the Si substrate. The stress is lessened by the ZnO buffer layer, so there is no such crack on the surface of sample A. On the other hand, the ZnO layer avoids the direct deposition of the polar ZnCdSe/ZnSe QWs on the nonpolar Si substrate. As is known, the direct deposition may lead to the imbalance in the interface charge and hinder the smooth growth of the QW^[7]. The above results demonstrate that the existence of a ZnO buffer layer enhances the quality of ZnCdSe/ZnSe QWs, which can also be seen from the following PL spectra.

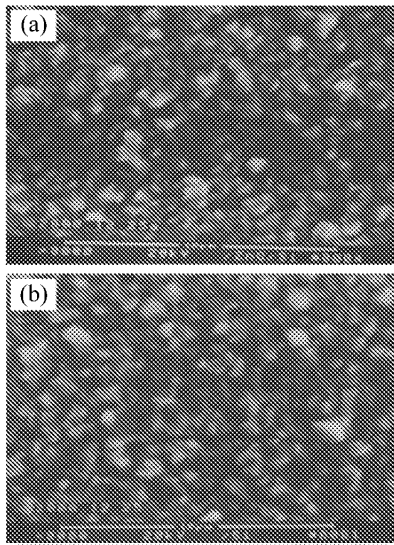


Fig. 1. Typical SEM micrographs of ZnCdSe/ZnSe QWs grown on Si (111) with (a) and without a ZnO buffer layer (b).

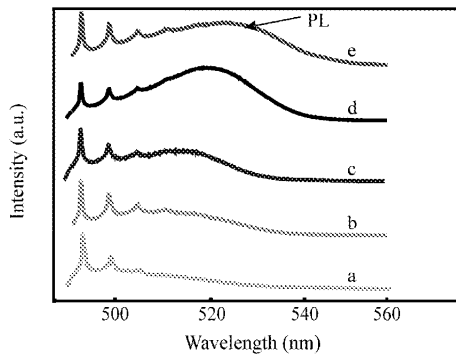


Fig. 2. The PL spectra of the ZnCdSe/ZnSe QWs with well widths of (a) 1.4, (b) 1.7, (c) 1.9, (d) 2.1 and (e) 2.4 nm, respectively, at room temperature (RT).

The most obvious character of PL spectra is that the spectra were overlapped by some sharp resonant Raman peaks on the high energy side of the emission line. The emission bands show a clear shift to lower energy as the well width is increased, while the Raman peaks remain unchanged.

According to Hill^[8], the band gap of $Zn_xCd_{1-x}Se$ can be expressed by

$$E_g(x) = E_{gCdSe} + (E_{gCdSe} - E_{gZnSe} - b)x + bx^2, \quad (1)$$

in which b is the bowing parameter and the value is 0.301^[9]. E_{gCdSe} and E_{gZnSe} are the band gaps of CdSe and ZnSe, respectively, with the values listed in Table 1. We can get the band gap of $Zn_{0.56}Cd_{0.44}Se$ of 2.17 eV based on Eq. (1).

Whereas the PL peak in Fig. 2 lies near 520 nm, there is a distinct difference from the calculated result. To verify the origin of the PL, we calculated the confinement energy of ZnCdSe/ZnSe QW with well width of 1.9 nm (sample c). Using the maximum of valence bands of ZnSe and CdSe and linearly interpolation^[10], one can get the valence band discontinuity of $Zn_{0.56}Cd_{0.44}Se$ well

Table 1. List of Parameters Used in the Calculation of the Electron and Hole Confinement Energies

	ZnSe	CdSe	$Zn_{0.56}Cd_{0.44}Se$
E_g (eV) (at RT)	2.7	1.67	2.173
m_e (m_0)	0.16	0.13	0.147
m_h (m_0)	0.6	0.45	0.534
$-E_{max}$ (eV)	10.58	10.35	10.479
E_x (meV)	17.4	15	16.3

E_g : the energy of band gap; m_e : the mass of electron; m_h : the mass of hole; $-E_{max}$: the maximum of valence bands; E_x : the exciton binding energy; m_0 : electron mass unit.

layer and ZnSe barrier layer of 0.101 eV. Accordingly, the conduction band discontinuity is 0.427 eV. The electron effective masses of ZnSe and CdSe are 0.13 and 0.16 m_0 , respectively. The hole effective masses of ZnSe and CdSe are 0.6 and 0.45 m_0 , respectively. Therefore, the electron and hole effective masses of ZnCdSe are 0.147 and 0.534 m_0 , respectively. The electron and hole confinement energies calculated by employing the finite-symmetry-potential quantum well model are 0.207 and 0.011 eV (the parameters used in the calculation can also be found in Table 1). Therefore, the calculated emission energy is $2.17 + 0.011 + 0.207 = 2.388$ eV (519 nm), which accords with the emission peak of sample c. So, the assignment of the emission peak from $Zn_{0.56}Cd_{0.44}Se$ is quite reasonable. Meanwhile, the $Zn_{0.56}Cd_{0.44}Se/ZnSe$ QWs grown directly on Si substrate did not exhibit any emission peak, that is likely due to the large difference in the interfacial chemistry between the epilayer and the substrate, which will lead to a larger dislocation density.

The dependence of the PL peak positions on well width of ZnCdSe/ZnSe QWs is shown in Fig. 3. The solid circles show the experimental results and the dash-dot line indicates the theoretical results calculated with the finite-symmetry-potential quantum well model considering the exciton binding energy. As can be seen from the figure, the theoretical result agrees quite well with the experimental data. This verifies again that the PL emission in our experiment comes from the ZnCdSe well layer.

The PL measurements of the QWs with well width of 2.4 nm at temperature range from 158 to 300 K are also carried out. Figure 4(a) shows the emission spectra of the structures and for simplicity, the spectra are normalized. Superimposed on the free exciton transition line is up

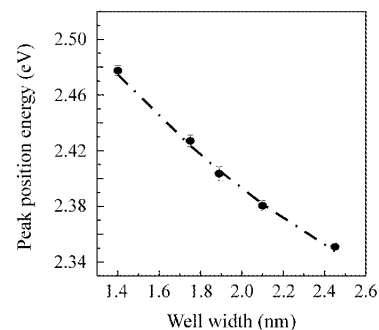


Fig. 3. Dependence of the peak positions on well width of ZnCdSe/ZnSe QW structures.

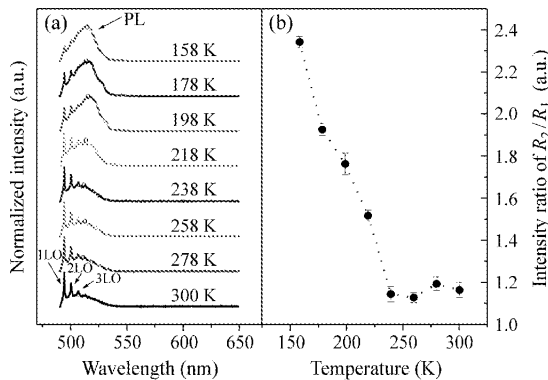


Fig. 4. (a) Normalized PL spectra of the QWs with well width of 2.4 nm at temperature range from 158 to 300 K; (b) the temperature dependent to R_2/R_1 (the intensity ratio of the 2LO peak to the 1LO peak).

to the third-order resonant Raman peaks. R_2/R_1 , the intensity ratio of the 2LO peak to the 1LO peak, decreases with increasing temperature, and keeps almost constant above 238 K, as shown in Fig. 4(b). Alivisatos *et al.*^[11] and M.C. Klein *et al.*^[12] reported on the resonant Raman scattering of $\text{CdS}_x\text{Se}_{1-x}$ nanocrystals, showing that the ratio of the first-order Raman peak to the second-order increases when the temperature is increased. Our experiment result is in accordance with the observations of aforementioned authors.

The Raman spectra of the abovementioned five QW structures were recorded in back-scattering configuration at RT and the results are shown in Fig. 5. The spectra have been normalized and shifted vertically for clarity. As can be seen from the figure, there appear three distinct Raman peaks in each spectrum, located near 254, 508, and 762 cm^{-1} , respectively. The energy interval of the peaks is about 254 cm^{-1} . The energy of them can be featured by the expression $n\omega_{\text{LO}}$ ($n = 1, 2, 3$), where ω_{LO} is the energy of longitudinal oscillation of a semiconductor lattice. It is noticeable that there is a shoulder on the high-energy side of the 2LO phonon. According to the peak position, it is attributed to the longitudinal optical (LO) phonon of silicon^[13].

In our experiment, the band frequencies of Raman peak (1LO) change from 254 up to 240 cm^{-1} with the change of the well width. We assign this peak to vibration frequency of a LO phonon of $\text{Zn}_{0.56}\text{Cd}_{0.44}\text{Se}$ for the following reasons: 1) When the value x is equal to 0.44, the LO mode in solid solution $\text{Zn}_{1-x}\text{Cd}_x\text{Se}$ is about 241 cm^{-1} accordingly^[14], it is near the experiment value. 2) Nakashima *et al.* argued that in the case of $\text{ZnCdSe}/\text{ZnSe}$ QWs, the LO wave-number of the CdZnSe well is blue shifted towards the wave-number of the ZnSe barrier^[15], whereas the LO phonon of the ZnSe barrier shows no shift because of the high fraction of unstrained material. 3) The Raman peak shows clear shift with well width, which provides further verification for our assignment of the Raman peak. The observable Raman peak of $\text{Zn}_{0.56}\text{Cd}_{0.44}\text{Se}$ QWs indicated the high quality of the sample with ZnO buffer layer.

The high quality $\text{ZnCdSe}/\text{ZnSe}$ QWs grown on silicon substrates with ZnO as a buffer layer were prepared by LP-MOVPE. The micrographs from SEM measurements indicate that the surface of the QWs is free of

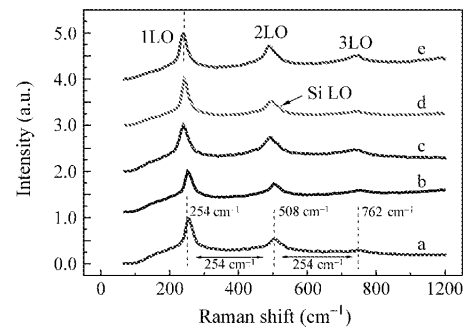


Fig. 5. The Raman spectra of the sample above mentioned.

microcracks, which proves that the incorporation existence of a ZnO layer enhanced the quality of the epilayer. The PL emission from $\text{ZnCdSe}/\text{ZnSe}$ QWs was obtained and discussed. The confinement energies of electrons and holes are calculated in terms of finite-symmetry-potential QW model and the calculated transition energies of the QWs structures agree well with the experimental results. The observation of Raman peak of ZnCdSe indicated that high quality QWs were fabricated with ZnO as a buffer layer.

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