Photoluminescence characteristics of ZnCdO/ZnO single quantum well grown by pulsed laser deposition

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Optical properties of ZnCdO/ZnO single quantum well (SQW) grown on c-sapphire substrate by pulsed laser deposition were investigated. Temperature dependent photoluminescence (PL) measurement was performed from 10 to 300 K to study the carrier localization effect and peak evolution. The LO-phonon replicas up to third order with Huang–Rhys factor of 0.17 were observed. The SQW exhibited very strong PL from the well layer and extremely weak emission from the ZnO barriers, indicating high quality interfaces and highly efficient relaxation. © *2011 American Institute of Physics*. [doi:10.1063/1.3567549]

ZnO-based semiconductor has been recognized as one of the most promising materials for high-efficiency light-emitting diodes and laser diodes operating in the blue and ultraviolet region.[1,2] In order to design ZnO-based devices, the realization of band gap engineering to create barrier layers and quantum wells (QWs) in device heterostructures is a crucial aspect.[3,4] By alloying with CdO that has a cubic structure and a narrower direct band gap of 2.3 eV, the band gap of ZnO can be redshifted toward blue or even green spectral region. Previously, ZnCdO/ZnO QWs have mainly been prepared by molecular beam epitaxy (MBE) and metal-organic epitaxial methods.[5–8] The growth of ZnCdO alloys by pulsed laser deposition (PLD) is difficult to realize because of the differences between the vapor pressures of Cd and Zn.[4,9–11] Moreover, CdO has a rock-salt structure, which is dissimilar to the wurtzite structure of ZnO. Thus, the growth of high crystalline quality ZnCdO QWs is rather difficult as defects in the well layer and interface barrier can usually be produced due to the complication of lattice mismatch. Therefore, a detailed study of excitons in ZnO-based QWs is important for understanding the optical properties of these heterostructures. However, very few reports have been published regarding the excitons of ZnCdO heterostructures.[11,12] In this letter, we report on the properties of excitonic luminescence and its LO-phonon replicas from ZnCdO/ZnO single QW (SQW) grown by PLD. The SQW exhibited very strong photoluminescence (PL) from the well layer with negligible emission from the ZnO barriers, indicating high quality interfaces and highly efficient relaxation.

ZnCdO/ZnO SQW was prepared on *c*-plane sapphire substrate by PLD in an ultrahigh vacuum chamber. The SQW consists of a 10 nm ZnO buffer layer, a ZnO barrier layer with thickness of 90 nm, a 2.6 nm $Zn_{1-x}Cd_xO$ (x=4.5%) well layer, and a ZnO cap layer thickness of 10 nm. Details of the growth procedures and the band gap energy in ZnCdO had been reported elsewhere.[13] A subsequent *in situ* post-deposition annealing treatment at 650 °C for 20 min was carried out to improve the quality of sample. Atomic force microscopy (AFM) and transmission electron microscopy (TEM) were employed to characterize the surface and the cross section of the sample, respectively. PL spectra were obtained with a 325 nm He–Cd laser excitation.

The cross-sectional schematic, AFM image of the surface, TEM image of a ZnCdO/ZnO SQW, and secondary ion mass spectrometry (SIMS) depth profile of Cd are shown in Figs. 1(a)–1(d), respectively. It is observed from Fig. 1(b) that atomically flat surface is formed on the SQW and the root mean square roughness over a scan area of $3\times3\ \mu m^2$ is 0.20 nm. As seen from Fig. 1(c), the sample presents hardly resolved interfaces between the well layer and barrier layers, which is ascribed to the perfect interfaces and the low Cd

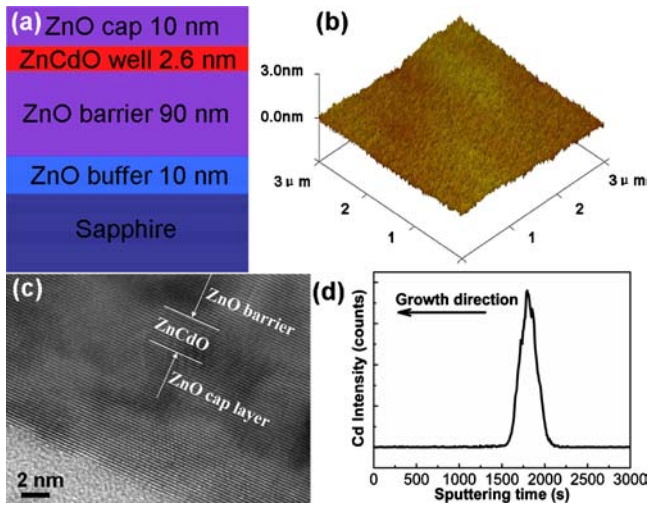

FIG. 1. (Color online) Cross-sectional schematic (a), AFM image of the surface (b), cross section TEM image (c) and, SIMS depth profile of Cd element (d) of the ZnCdO/ZnO SQW.

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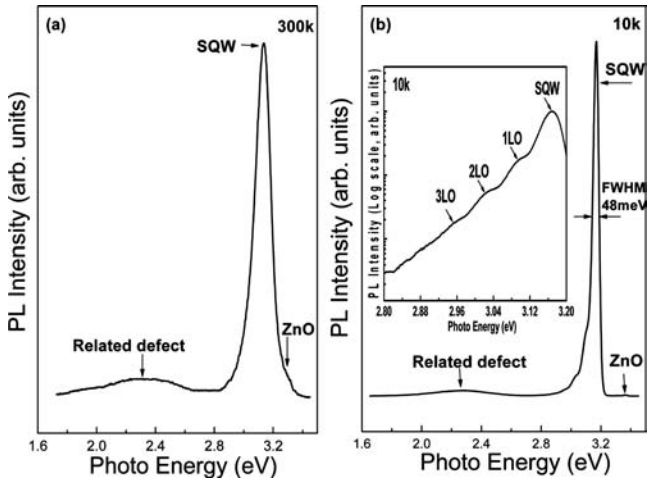

FIG. 2. PL spectra of ZnCdO/ZnO SQW measured at (a) room temperature and (b) 10 K. The inset of (b) is high resolution PL spectrum of the sample.

concentration in the well layer. A perfect interface is key to the growth of high quality QW, and perfect interfaces achieved in the SQW are proposed to be ascribed to the low lattice mismatch, as the result of low Cd doping.[4] Moreover, the smooth surface of both ZnO barriers and ZnCdO well and the postannealing treatment also contribute to the high quality interfaces. The existence of SQW structure is confirmed by the existence of a Cd peak in the SIMS depth profile as shown in Fig. 1(d).

Figure 2 shows PL spectra of the ZnCdO/ZnO SQW at room temperature and 10 K. The inset of Fig. 2(b) is the high resolution PL spectrum of the sample. In Figs. 2(a) and 2(b), the peak at 3.14 eV is from the exciton transition confined in ZnCdO well, the inconspicuous peak emission around 3.28 eV corresponds to the emissions from ZnO barriers, and a broad band defect-related luminescence around 2.3 eV is related to oxygen vacancies or zinc interstitials.[14,15] It is observed that the SQW exhibited very strong PL from the well layer, while extremely weak emission from deep level defects and the ZnO barriers both at room temperature and 10 K. This high-efficiency relaxation from barrier to well layer implies that perfectly smooth interfaces in the ZnCdO/ZnO SQW have been achieved by PLD. Thus, most photon-generated carriers in the ZnO barrier level relax into the ZnCdO well level without any obstruction, leading to very strong emission from well layer. This is in good agreement with the analysis of AFM and TEM results above. In addition, it is interesting to note from Fig. 2(b) inset that LO-phonon replicas up to three orders of the exciton band can be easily resolved from the 10 K PL spectrum, also indicating the high crystalline quality of the sample. In the Franck–Condon model, the coupling strength between the radiative transition and the LO-phonon can be characterized by the Huang–Rhys factor S.[16] The relative intensity of the nth phonon replica I_n is related to the zero-phonon peak I_0 by the S factor through $I_n = I_0(S^n/n!)$, where n is a natural number. From the measured spectrum, the S factor associated with our SQW excitons is estimated to be 0.17. On the other hand, the low temperature width of this SQW emission is as small as 48 meV, which is three times smaller than QWs of comparable structures grown on a-plane sapphire substrates by MBE.[17] It is known that narrow lines in luminescence of QW excitons at low temperatures implies high quality of QW interfaces.[18] All these results indicate that the high quality

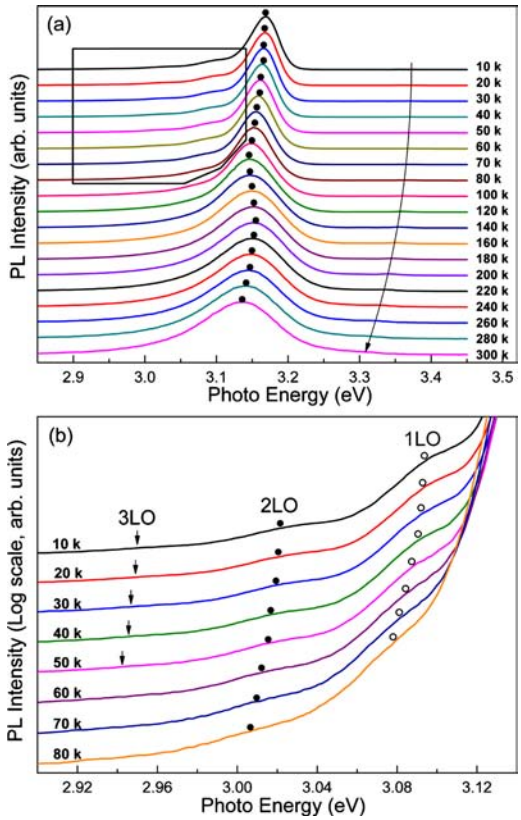

FIG. 3. (Color online) (a) Normalized PL spectrum (linear scale) of the ZnCdO/ZnO SQW at various temperatures. The close circles and the solid line indicate the peak evolution of the QW-related emission and the FX_A emission of ZnO barriers, respectively. (b) Temperature dependence of the spectra (logarithmic scale) of LO-phonon replicas of SQW, namely the designated area in (a).

ZnCdO/ZnO SQW with high-efficiency relaxation from the barrier to well layer have been achieved in our case, which is ascribed to the perfectly smooth interfaces, as a consequence of a combined effect of low lattice mismatch, appropriate growth control, and the postdeposition annealing treatment.

To further investigate the effect of exciton localization in the SQW, temperature dependent PL spectra were collected. The normalized PL spectra for the sample measured from 10 to 300 K are presented in Fig. 3. We observe that the peak energy of the QW-related emission shows an inconspicuous S-shaped property due to the weak carrier localization effect, which can be ascribed to a combined effect of the slightly disordered ZnCdO alloy and smooth interfaces between the well and ZnO barriers. A typical S-shaped behavior has been observed previously in the ZnO/ZnCdO/ZnO double heterostructures[11] and GaN-based QWs (Ref. 19) with strong carrier localization effect, which is ascribed to the potential fluctuation, as a consequence of the inhomogeneous alloy composition and roughness interface.

Figure 4 shows the variation in the PL peak energies and the integrated PL intensity of the QW-related emission of the ZnCdO/ZnO SQW as a function of temperature. It is found that the FX_A, D^0X, and -LO peak energies show a monotonic redshift with increasing temperature. The FX_A peak energy decreases monotonically with increasing temperature, which can be well described by the empirical Varshni equation: $E(T) = E(0) - \alpha T^2/(\beta + T)$, where $E(0)$ is the excitonic band gap at 0 K, and α and β are the corresponding thermal coefficients. The closed squares in Fig. 4(a) are the experimen-

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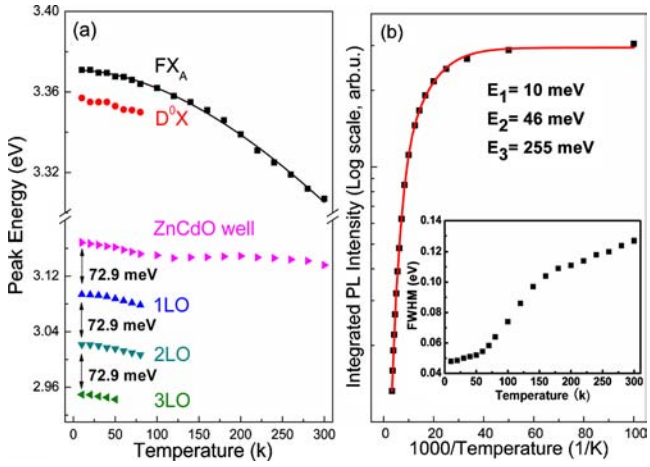

FIG. 4. (Color online) (a) Temperature dependent peak positions of FX_A, D^0X, SQW, and its 1LO-, 2LO-, and 3LO-phonon replicas. The solid line is the fitting curve of the experimental data according to Varshni equation. (b) Dependence of the integrated PL intensity on the reciprocal of temperature, the solid curve is the corresponding fit based on Eq. (1). The inset of (b) is the evolution of the FWHM of the QW PL band with temperature.

tal data of FX_A peak energy and the black lines are the fitting curve obtained by using the Varshni's equation. It is clearly shown that the curves fit our experimental data very well. The value of $E(0)$ obtained from the fitting is 3.37 eV, with $\alpha=7.9\times10^{-4}$ eV/K and $\beta=789$ K. On the other hand, it clearly shows that the energy difference between QW emission and its LO-phonon replicas is well defined to be 72.9 meV, slightly larger than the phonon energy reported in ZnO.[20] Moreover, as seen from Fig. 4(b), the intensity of the ZnCdO QW-related emission decreases remarkably with increasing temperature, which is partly due to the increased nonradiative recombination. In general, the temperature dependent PL intensity of a QW is described by a modified three channel Arrhenius fit function[21,22]

$$I(T)=\frac{I(0)}{1+C_1\exp(-E_1/kT)+C_2\exp(-E_2/kT)+C_3\exp(-E_3/kT)}, \quad (1)$$

where $I(T)$ is the integrated PL intensity at temperature T, k is the Boltzmann constant, E denotes the activation energy, C is a tunneling factor, and $I(0)$ is the integrated intensity at the low temperature limit. The solid line in Fig. 4(b) is the fitting to the variations using Eq. (1) for the localized excitons intensity. As shown in Fig. 4(b), the localized excitons intensity is described well using the three processes with different activation energies, where the three activation energies are corresponding to a localization energy or ionization energy of donor bound excitons ($E_1=10$ meV), an exciton binding energy ($E_2=46$ meV), and an activation energy for a carrier escaping into the surrounding ZnO barriers ($E_3=255$ meV). In general, the lowest activation energy E_1 can be due to either the ionized donor bound excitons[22] or the thermionic emission of the localized excitons out of the potential minima[21] caused by interface fluctuations and inhomogeneous alloy composition. Since the interfaces in the SQW are of a good quality as we demonstrated above, the influence of potential minima localizing excitons caused by interface fluctuations would be negligible. Here, we deduced that this activation energy is ascribed to exciton localization in potential minima of the slightly disordered ZnCdO alloy or ionized donor bound excitons within the ZnCdO/ZnO SQW. On the other hand, it was found that the linewidth of the QW PL peak shows a W-shape with increasing temperature from 10 to 300 K [shown in the inset of Fig. 4(b)], which is a well-known manifestation of phonon-assisted motion of localized excitons (hopping).[8]

In summary, we have investigated temperature dependence of excitonic PL from a ZnCdO/ZnO SQW grown on sapphire substrate by PLD. The peak energy of the QW-related luminescence shows a weak localization effect of excitons as a function of temperature. The LO-phonon replicas up to third order with Huang–Rhys factor of 0.17 are observed. The SQW exhibited very strong PL from the well layer, while the emission from ZnO barriers was extremely weak, indicating the high quality interfaces and highly efficient relaxation.

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