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Pulsed laser deposition of high-quality ZnCdO epilayers and ZnCdO/ZnO single quantum well on sapphire substrate

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The authors report on high quality ZnCdO alloy epilayers and ZnCdO/ZnO single quantum well structures on sapphire substrates by pulsed laser deposition. The Cd concentration in the ZnCdO alloy can be systematically adjusted via the substrate temperature and single-phase ZnCdO alloy with a band gap at room temperature extended to 2.94 eV is achieved. The single quantum well structures exhibit strong photoluminescence from the well layer with extremely weak emission from deep level defects and the ZnO barrier, indicating the high quality of ZnCdO/ZnO single quantum well structures. © *2010 American Institute of Physics*. [doi:10.1063/1.3478006]

ZnO-based semiconductors have been recognized as the most promising materials for high efficiency light-emitting diodes (LEDs) and laser diodes (LDs) operating in the blue and ultraviolet region,[1–3] owing to their direct wide band gap (3.37 eV) and large binding energy of excitons (60 meV). An important issue in optoelectronic devices especially LEDs and LDs with high emitting efficiency is the band gap engineering to form quantum wells (QWs).[4–10] Redshift in the luminescence peak with respect to that of ZnO can be realized by alloying ZnO with CdO. However, CdO assumes the rock-salt structure, which is dissimilar to the wurtzite structure of ZnO. This is indeed a problem for ZnCdO alloys with high content of Cd, where poor crystalline quality and phase separation are expected to occur. Previously, ZnCdO epilayers and ZnCdO/ZnO QWs have been mainly prepared by molecular beam epitaxy and metal-organic epitaxial methods.[11–20] In comparison, pulsed laser deposition (PLD) is a widely used and versatile technique that allows us to monitor the growth by controlling properly relevant growth parameters like laser power and pulse frequency, substrate temperature, deposition rate, material composition, etc. However, up till now, the fabrication of ZnCdO films and heterostructures by PLD is rarely reported.[7,21,22] Makino *et al.*[7] were able to introduce up to 7% Cd into single-phase $Zn_{1-x}Cd_xO$ layers grown on lattice-matched $ScAlMgO_4$ substrates by PLD. However, Cd composition in $Zn_{1-x}Cd_xO$ films exceeding $x=7\%$ has not be so far achieved. In this letter, we represent a low-temperature growth approach to the fabrication of high-quality ZnCdO films and single QW (SQW) using PLD on commonly used sapphire substrates.

ZnCdO films and ZnCdO/ZnO SQW were prepared on *c*-plane sapphire substrates by PLD method. A KrF excimer laser (248 nm, 320 mJ, 20 Hz, and 25 ns) was used as ablating source and two ceramic targets of ZnO and $Zn_{0.7}Cd_{0.3}O$ were used. Before being loaded into the growth chamber, the sapphire substrates were cleaned in acetone, ethanol and deionized water. The ZnCdO films (~200 nm in thickness) were grown in 2×10^{-3} Torr of pure oxygen and in the substrate temperature range of 180–600 °C. Moreover, two ZnCdO/ZnO SQWs with the same well width of 2.6 nm but different Cd contents were fabricated. The SQWs consist of a 10 nm ZnO buffer layer, a ZnO barrier layer with thickness of 90 nm, a 2.6 nm ZnCdO well layer, and a ZnO cap layer thickness of 10 nm. The subsequent annealing treatment *in situ* at 650 °C for 20 min was carried out to improve the interface between ZnO barrier and ZnCdO well layer. The Cd contents were determined by energy-dispersive x-ray spectroscopy (EDS) analysis. The barrier and well layer thicknesses were determined by prescribed deposition time. High resolution x-ray diffraction (HRXRD) and atomic force microscopy (AFM) are employed to characterize the crystalline quality and the surface morphology of the samples, respectively. The photoluminescence (PL) spectra were performed by excitation from a 325 nm line from a He–Cd laser.

Figure 1(a) presents various Cd content of ZnCdO layers grown at various substrate temperature (180–600 °C). The Cd content decreases orderly with increasing substrate temperature. Experimentally, we can modify the Cd percentage of the $Zn_{1-x}Cd_xO$ film through controlling the substrate temperature. Due to substantially reduced desorption rates of Cd, Cd-rich growth conditions are favored in low-temperature substrate. In this experiment, the maximum Cd content of ZnCdO film grown on 180 °C substrate was up to about 8.7 at. % without a CdO phase separation, which was significantly larger than the thermodynamic solid solubility limits (2 at. %).[22] However, the Cd contents in the alloyed films were much lower than those in the targets, due to the difference between the vapor pressures of Cd and Zn. Here we need to mention that further increase of the Cd content in ZnCdO films should be possible upon optimized growth conditions by tuning the substrate temperature, laser power, and chamber pressure etc.

Figure 1(b) shows HRXRD patterns of $Zn_{1-x}Cd_xO$ film ($x=8.7\%$) grown on *c*-plane sapphire substrate. A very strong diffraction peak from the *c*-plane (0001) Al_2O_3 substrate and a peak (0002) from wurtzite ZnCdO phase were observed. The AFM images of ZnCdO film and ZnCdO/ZnO SQW are shown in Figs. 1(c) and 1(d). It is observed that atomically flat islands with the scales of several tens of nm in width and ~1 nm in height are formed on the ZnCdO film. The root mean square roughness over a scan area of 3×3 μm^2 is 0.68 nm for ZnCdO film and 0.26 nm for SQW, respectively.

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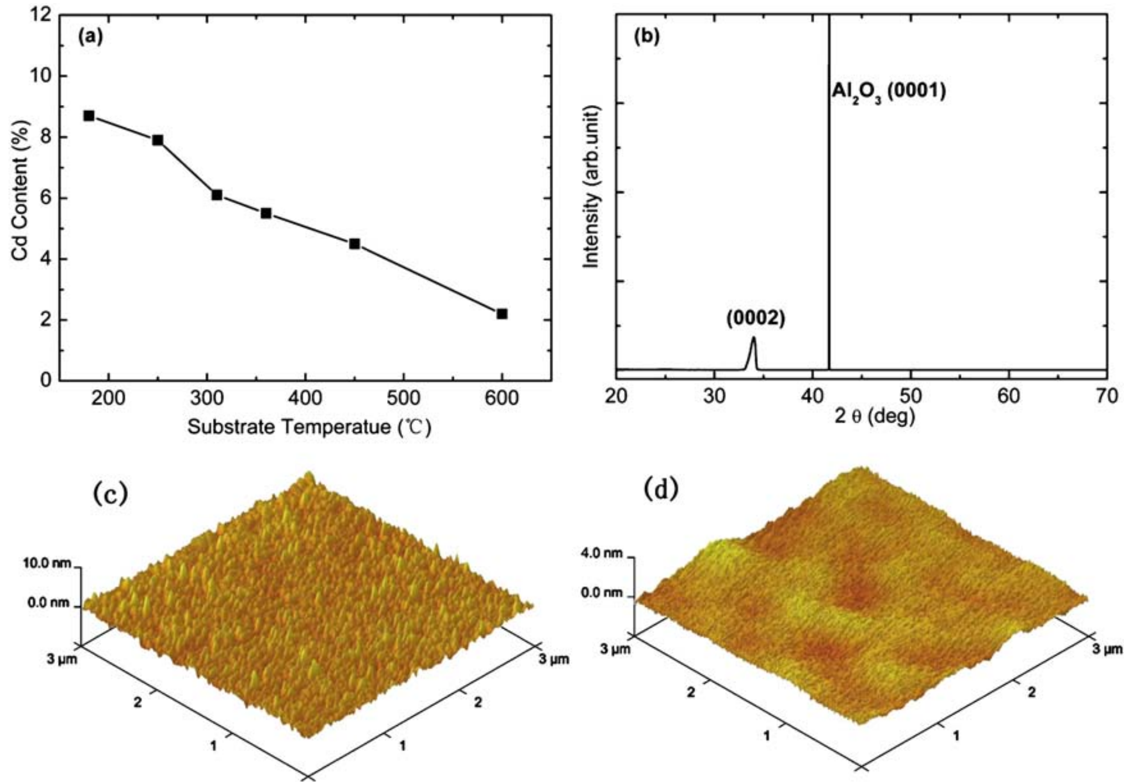

FIG. 1. (Color online) (a) Cd content vs substrate temperature deduced from EDS. (b) HRXRD pattern of the $Zn_{1-x}Cd_xO$ film (x=8.7%) on *c*-plane (0001) sapphire substrate. [(c) and (d)] AFM image of the surface of $Zn_{1-x}Cd_xO$ film and $Zn_{1-x}Cd_xO/ZnO$ SQW (x=7.9%), respectively.

Optical transmittance and PL spectra of ZnCdO films with four representative Cd contents at room temperature are shown in Figs. 2(a) and 2(b). All epilayers exhibit strong band gap related emission under optical excitation at room temperature. PL peak of ZnCdO shifts toward lower energy along lower-energy-shift of absorption edge with increasing Cd content. The optical band gap (E_g) of the films were extracted from transmission spectra by plotting α^2 (the optical absorption coefficient) versus $h\nu$ and extrapolating the linear portion of this plot to the energy axis. The band gap energy of $Zn_{1-x}Cd_xO$ films at room temperature as a function of alloy content is shown in the inset of Fig. 2(a). Band gap extending to 2.94 eV could be achieved by incorporating Cd with x=8.7%. The experimental data can be well fitted using the conventional expression $E_g^{CdZnO}=xE_g^{CdO}+(1-x)E_g^{ZnO}-bx(1-x)$, where b is the bowing parameter, and E_g^{CdO} and E_g^{ZnO} are the band gaps of compounds CdO (2.3 eV) and ZnO, respectively. By fitting the calculated optical band gap, the bowing parameter b of 3.43 eV can be obtained, which is greater than the recent reported values of 0.95 and 1.21 eV.[14,23] However, it is less than the previous results of 5.95 and 8.12 eV,[7,20] which is calculated by optical reflectivity and absorption data deduced from polynomial fitting. We need to point out that the discrepancy may be ascribed to the neglect of the excitonic contributions of optical absorption edge,[14] and also to the optical band tail induced by the density of states of localization.[22]

Figure 3 shows PL spectra of the two single ZnCdO/ZnO QW structures with the same well width of 2.6 nm but different Cd contents of (1) 4.5% and (2) 7.9%. In order to control the Cd content in the well layers, ZnCdO layers were grown at low substrate temperature of 250 and 450 °C. After the growth of ZnO cap layer, an *in situ* annealing at 650 °C has been carried out to improve the quality of ZnCdO well layer and the interface. Figures 3(a) and 3(b) show the PL spectra of the high Cd content SQW at 10 K and room temperature, respectively. Judging from the peak positions [Fig. 3(b)], one peak at 3.0 eV is from the exciton transition confined in ZnCdO well layer, and the emission around 3.28 eV can be ascribed to the emission from ZnO barrier. On the low energy side, a broad band defect-related luminescence around 2.3 eV was observed, which is related to deep level defects. These deep levels are most probably due to oxygen vacancies or zinc interstitials,[24,25] which should be the dominating sources of the defect emission for the SQW analyzed in this work. On the other hand, the spectrally integrated yield of the QW emission in the x=7.9% structure is even much larger than that from the ZnO barrier despite ~40 times larger total thickness of ZnO, both at low and room temperatures.

For lower Cd content [Figs. 3(c) and 3(d)], emission from well layer dominates in the PL spectrum and emission from the defects and barriers are extremely weak, which implies that the perfectly smooth interfaces between well and barrier layer have been achieved in this SQW. Thus, most photon-generated carriers in the ZnO barrier level relax into the ZnCdO well level, leading to strong emission from well layer. On the other hand, the low-temperature width of this QW emission is as small as 48 meV. This value is about three times smaller than QWs of comparable structures grown on *a*-plane sapphire substrates by molecular beam epitaxy.[26] The broader PL linewidth from the higher Cd SQW results from the inhomogeneous broadening due to the larger composition fluctuation and degraded well layer quality and the interfaces. As mentioned above, CdO assumes the rock-salt structure, different from the wurtzite structure of ZnO. The

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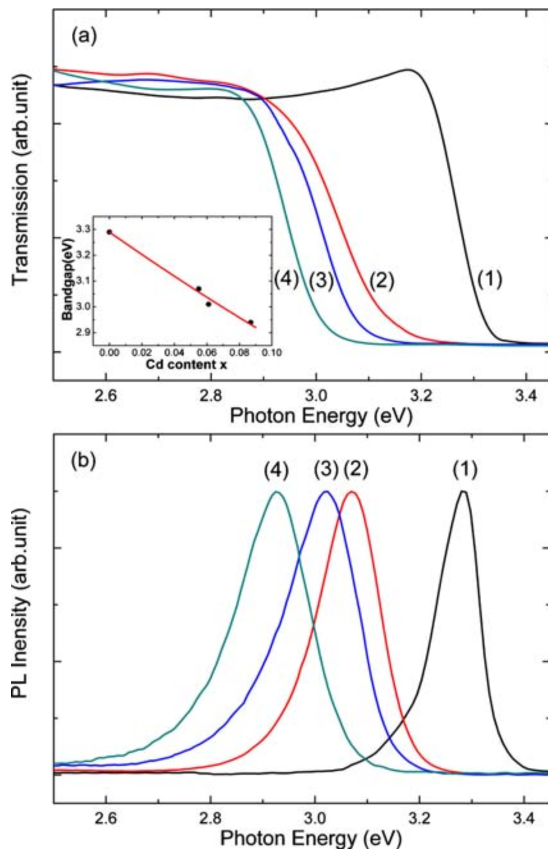

FIG. 2. (Color online) Transmission (a) and PL spectra (b) of ZnCdO epilayers at room temperature. The Cd content increases from the right to the left: (1) 0%, (2) 5.5%, (3) 6.1%, and (4) 8.7%. Transmission spectra are tested by the same PL system and the light source is a xenon lamp. The inset of (a) shows the variation in band gap energy as a function of Cd content. The black dots represent experimental data. The red line is a fitting curve using the equation $E_g^{CdZnO}=xE_g^{CdO}+(1-x)E_g^{ZnO}-bx(1-x)$.

growth of higher Cd content well layer with high crystalline quality is rather difficult and it usually produces defects in the well layer and interface state between the well and barriers caused by Cd substitutional impurities. This is in good agreement with the results that the defect-related emission from the higher Cd sample is stronger than from the lower sample.

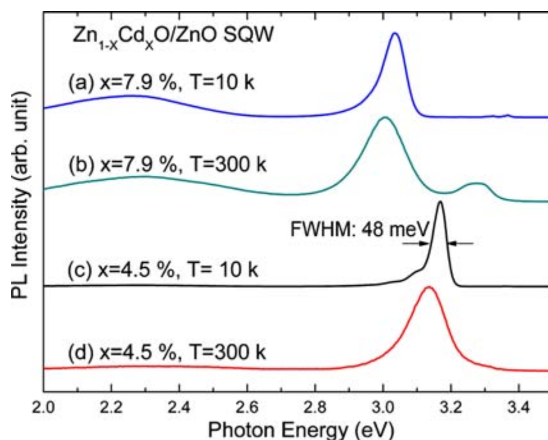

FIG. 3. (Color online) PL spectra of ZnCdO/ZnO SQW structures measured at 10 K and room temperature excited by a He–Cd laser. Two samples with the various Cd contents in $Zn_{1-x}Cd_xO$ well layer of 4.5% and 7.9% are shown.

In summary, high quality ZnCdO/ZnO film and SQWs were grown on sapphire substrates by PLD. We were able to introduce up to 8.7% Cd into ZnCdO layers grown on sapphire substrates, resulting in a narrowing band gap of 2.94 eV. The strong well layer emission with extremely weak barrier layer emission from the SQW implies that high quality ZnCdO/ZnO SQW structures with smooth interfaces have been grown on sapphire. Since PLD is a widely used technique and since sapphire is much cheaper than other lattice-matched substrates, this work represents a significant development of ZnO-based optoelectronic devices.

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