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Temperature-dependent photoluminescence of CdZnO thin films grown by molecular-beam epitaxy

Z. Yang, L. Li, Z. Zuo, J.L. Liu *

Quantum Structures Laboratory, Department of Electrical Engineering, University of California, Riverside, CA 92521, USA

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ABSTRACT

Large-Cd-concentration ($E_g < 3.0\,\text{eV}$) CdZnO thin films were grown using molecular-beam epitaxy. Variable-temperature photoluminescence measurements were performed on three typical CdZnO samples having pure wurtzite, pure rocksalt, and wurtzite–rocksalt mixture structures, respectively. The temperature dependence of the CdZnO bandgap shrinkage was investigated and analyzed based on the empirical Varshni and Bose–Einstein fitting on the near-band-edge photoluminescence peak positions. The temperature dependence of the integral PL intensity in the CdZnO samples was also fitted, where fitting equation with hopping term included shows a closer fit to the experimental data. The possible hopping processes in the CdZnO thin films may be related to the band tail states due to alloying effect and Cd distribution nonuniformity in the CdZnO samples.

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1. Introduction

Cd can be alloyed into ZnO to narrow its bandgap [1–3], for extending the optoelectronic applications of ZnO from near ultraviolet to longer wavelength in the visible region. However, due to the difficulties in alloying large amounts of Cd into ZnO [1], CdZnO materials with bandgap smaller than 3.0 eV have not been achieved for a long time until recently [4–7]. Consequently, comprehensive studies on large-Cd-concentration CdZnO ($E_g < 3.0$ eV) materials were rarely reported compared to the studies of small-Cd-concentration CdZnO materials [8–16]. In particular, the temperature-dependent photoluminescence (PL) studies of CdZnO materials with bandgap reaching the visible region were rarely reported, although these studies are critically important to extract material parameters for future device applications such as light-emitting devices with CdZnO as active layers. In this paper, the temperature dependence of the bandgap change and PL thermal quenching mechanism in the CdZnO thin films were investigated and analyzed based on the variable-temperature PL studies of typical wurtzite (*wz*) CdZnO, rocksalt (*rs*) CdZnO and mixture-structural CdZnO thin film samples.

2. Experiment

CdZnO thin films were grown on Si (1 0 0) substrates using plasma-assisted molecular-beam epitaxy (MBE). The Si substrates were dipped into Piranha solution (H_2SO_4:H_2O_2=5:3) and diluted HF alternately for 1 min each for 3 times for surface cleaning, rinsed by de-ionized water in between and after, and finally dried by nitrogen gun before being transferred into an MBE intro-chamber. Elemental Zn (6N) and Cd (6N) heated by regular Knudsen effusion cells were used as zinc and cadmium sources. Oxygen (5N) plasma generated by a radiofrequency plasma generator was used as the oxygen source. Extremely low growth temperatures ranging from 120 to 200 °C were employed in order to achieve a large amount of Cd incorporation into ZnO. A thin ZnO buffer layer (10–20 nm) was grown before CdZnO growth for each sample. The thickness of the CdZnO layer is 100–200 nm. Energy dispersive X-ray (EDX) spectroscopy was performed using a Philips XL 30 FEG scanning electron microscope. Based on the EDX measurements, the Cd concentration is approximately estimated to be 2.5%, 8.1%, and 25.8% in CdZnO samples A, B, and C discussed in this paper. X-ray diffraction (XRD) measurements were carried out using a Bruker D8 Advance X-ray diffractometer. PL measurements were performed using a home-built system. A He–Cd laser of 325 nm wavelength was used as an excitation source and a photomultiplier tube was used to detect the PL signals. The temperature control from 9 to 300 K was achieved by a Janis cryostat equipped with a He compressor.

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* Corresponding author. Tel.: +1 951 8277131; fax: +1 951 8272425.
E-mail address: jianlin@ee.ucr.edu (J.L. Liu).

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3. Results and discussions

Fig. 1(a)–(c) shows the XRD patterns of CdZnO samples A–C, respectively. Sample A only shows a wurtzite (*wz*) CdZnO (0 0 0 2) peak at $2\theta = 34.5^\circ$ and sample C only shows a broad rocksalt (*rs*) CdZnO (1 0 0) peak at $2\theta = 17.5^\circ$, indicating pure *wz* and *rs*

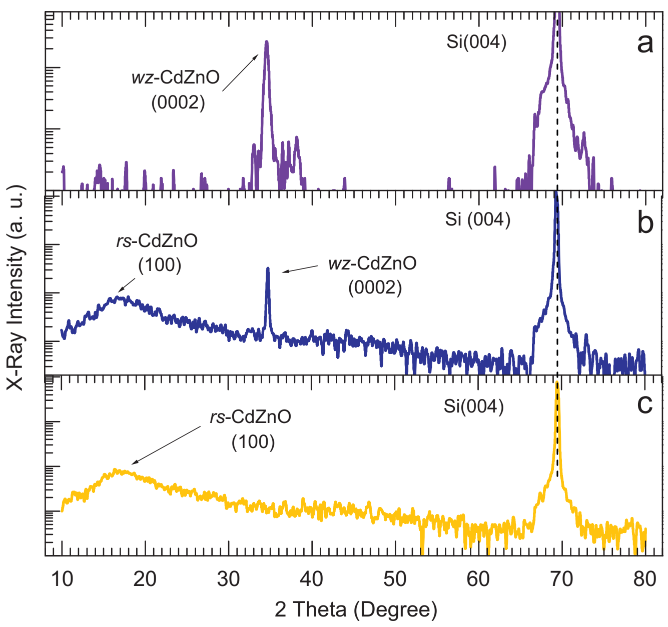

Fig. 1. X-ray diffraction patterns of (a) *wz*–CdZnO sample A, (b) *wzrs*–CdZnO sample B, and (c) *rs*–CdZnO sample C. The intensity is in logarithmic scale.

Table 1
Photoluminescence peak positions and colors of the samples at 300 K.

Sample no.	Description	PL peak position at 300 K		
		(eV)	(nm)	Color
U	ZnO	3.287	377	UV
A	*wz*–CdZnO	2.863	433	Violet
B	*wzrs*–CdZnO	2.690	461	Blue
C	*rs*–CdZnO	2.156	575	Yellow

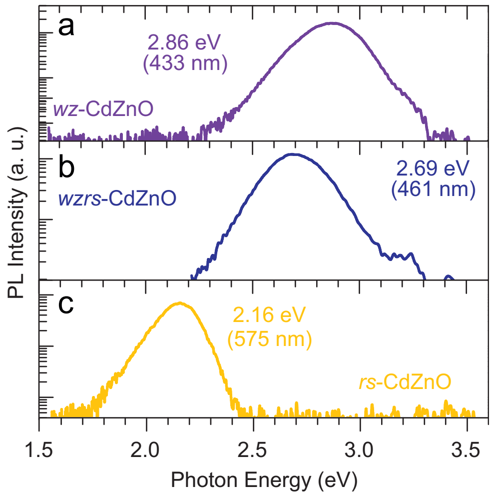

Fig. 2. Room-temperature PL spectra of (a) *wz*–CdZnO sample A, (b) *wzrs*–CdZnO sample B, and (c) *rs*–CdZnO sample C. The intensity is in logarithmic scale.

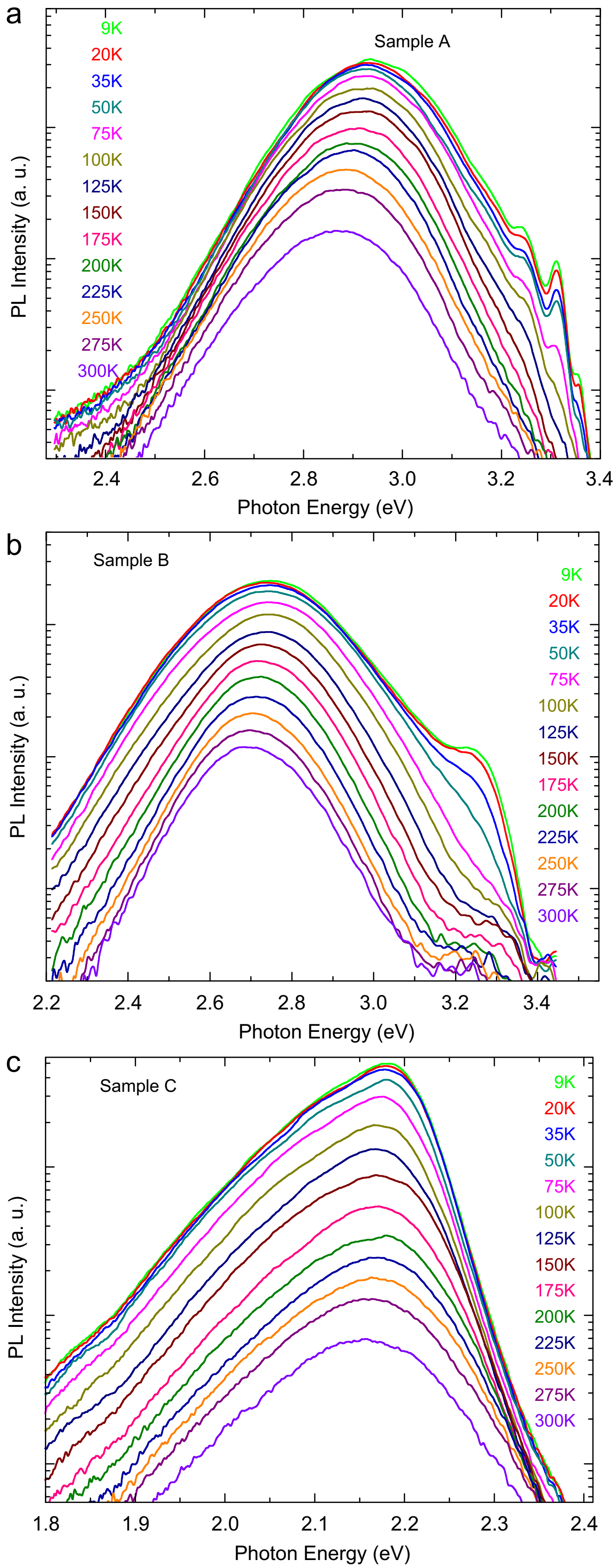

Fig. 3. Temperature-dependent PL spectra of (a) *wz*–CdZnO sample A, (b) *wzrs*–CdZnO sample B, and (c) *rs*–CdZnO sample C from 9 to 300 K. The intensity is in logarithmic scale.

structures, respectively. However, sample B shows both *wz*-CdZnO (0002) and *rs*-CdZnO (1 0 0) peaks in the XRD curve, indicating the phase segregation and mixture of *wz* and *rs* structure. The broadness of the *rs*–CdZnO (1 0 0) peak is possibly due to the low crystallinity of the *rs* phase in the CdZnO samples. In the XRD patterns, Si substrate (0 0 4) peaks at $2\theta = 69.5^\circ$ were also observed in all three samples. The crystal structures of the samples are also summarized in the sample description column of Table 1 , where "*wzrs*" represents a mixture structure of wurtzite and rocksalt.

Fig. 2(a)–(c) shows the room-temperature (RT) PL spectra of CdZnO samples A–C, respectively. The RT PL peak position of samples A, B and C locate at 2.863 (433 nm), 2.690 (461 nm) and 2.156 eV (575 nm), respectively, which are all attributed to the near-band-edge (NBE) emissions in these CdZnO thin films. The 300 K PL peak positions of the samples are also summarized in Table 1.

Fig. 3(a)–(c) shows the temperature-dependent PL spectra of *wz*-CdZnO (sample A), *wzrs*–CdZnO (sample B), and *rs*–CdZnO (sample C). The broad CdZnO NBE PL peaks red-shifted from 2.922 to 2.863 eV in sample A, from 2.741 to 2.690 eV in sample B, and from 2.179 to 2.156 eV in sample C with temperature increasing from 9 to 300 K, respectively. The red-shifts are attributed to the bandgap shrinkage of the CdZnO with increasing temperature. The temperature-dependent PL peak shift values of the CdZnO samples are summarized in Table 2. The bandgap shrinkage in *wz*–CdZnO (59 meV) is slightly smaller than the value of ZnO (84 meV), while *rs*–CdZnO shows a significantly smaller bandgap shrinkage (23 meV) compared to the ZnO and *wz*–CdZnO sample. Besides the broad peaks arising from the CdZnO NBE emission, high-energy (~3.3 eV) PL peaks were also observed in Fig. 3(a) and (b), which are associated with the PL emissions from ZnO buffer layers.

Temperature dependence of the NBE PL peak positions in CdZnO samples A, B, and C was fitted by both the Varshni relation [17]

$$E_g(T) = E_g(0) - \frac{\alpha T^2}{T+\beta} \tag{1}$$

and the Bose–Einstein (B–E) bandgap relation [18,19]

$$E_g(T) = E_g(0) - \frac{k}{\exp(\theta/T) - 1} \tag{2}$$

In the relations, $E_g(0)$ is the bandgap at 0 K, and α, β, k, and θ are fitting parameters. The fitting parameters are shown in Table 2. Fig. 4 shows the Varshni fitting (red line) and B–E fitting (blue line) on the temperature dependence of the PL peak energy positions in *wz*–CdZnO, *wzrs*–CdZnO, *rs*–CdZnO, and a reference ZnO sample. In Varshni fitting, *wz*–CdZnO shows relatively close fitting parameters to ZnO; however, the fitting parameters of *rs*–CdZnO vary significantly with ZnO and *wz*–CdZnO. In B–E fitting, the fitting parameters of *wz*–CdZnO and *rs*–CdZnO are relatively close to each other, but quite different from the fitting parameters of reference ZnO and *wzrs*–CdZnO samples. The fitting parameters shown in Table 2 may be used for estimating wavelength reliability on temperature of future CdZnO light-emitting devices. The weaker temperature dependence of the bandgap shrinkage in CdZnO than ZnO implies a robuster thermal stability of the emitting-light wavelength from the CdZnO device.

Fig. 5 shows the fitting on the temperature dependence of the integral PL peak intensities in ZnO sample U and CdZnO samples A–C. The red lines show the fitting using the general PL intensity thermal quenching relation [20–23],

$$\frac{I(T)}{I_0} = \frac{1}{1 + c\exp(-E_a/k_BT)} \tag{3}$$

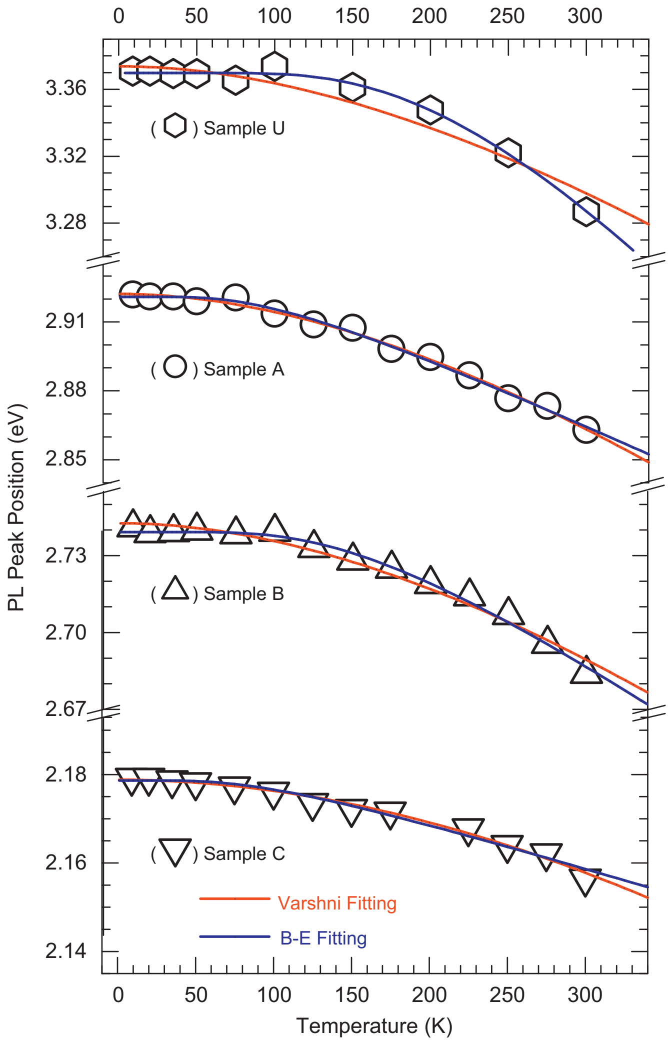

Fig. 4. Varshni fitting (red line) and B–E fitting (blue line) on the temperature dependence of the PL peak energy positions in *wz*–CdZnO sample A, *wzrs*–CdZnO sample B, *rs*–CdZnO sample C, and ZnO sample U. (For interpretation of the references to colour in the figure legend, the reader is referred to the web version of this article.)

Table 2
Photoluminescence peak shifts, Varshni and B–E fitting parameters on the temperature dependence of the bandgap in CdZnO and ZnO samples.

No.	$\Delta E = E_{9\,\mathrm{K}} - E_{300\,\mathrm{K}}$			$E_g(T) = E_g(0) - \frac{\alpha T^2}{T+\beta}$			$E_g(T) = E_g(0) - \frac{k}{\exp(\theta/T)-1}$		
	$E_{300\,\mathrm{K}}$ (eV)	$E_{9\,\mathrm{K}}$ (eV)	ΔE (meV)	$E_g(0)$ (eV)	α (meV/K)	β (K)	$E_g(0)$ (eV)	k (meV)	θ (K)
U	3.287	3.371	84	3.374	0.998	882	3.370	913	64.7
A	2.863	2.922	59	2.922	0.781	891	2.921	93.5	25.4
B	2.690	2.741	57	2.743	0.741	950	2.739	230	43.7
C	2.156	2.179	23	2.179	0.740	2867	2.179	29.8	23.7

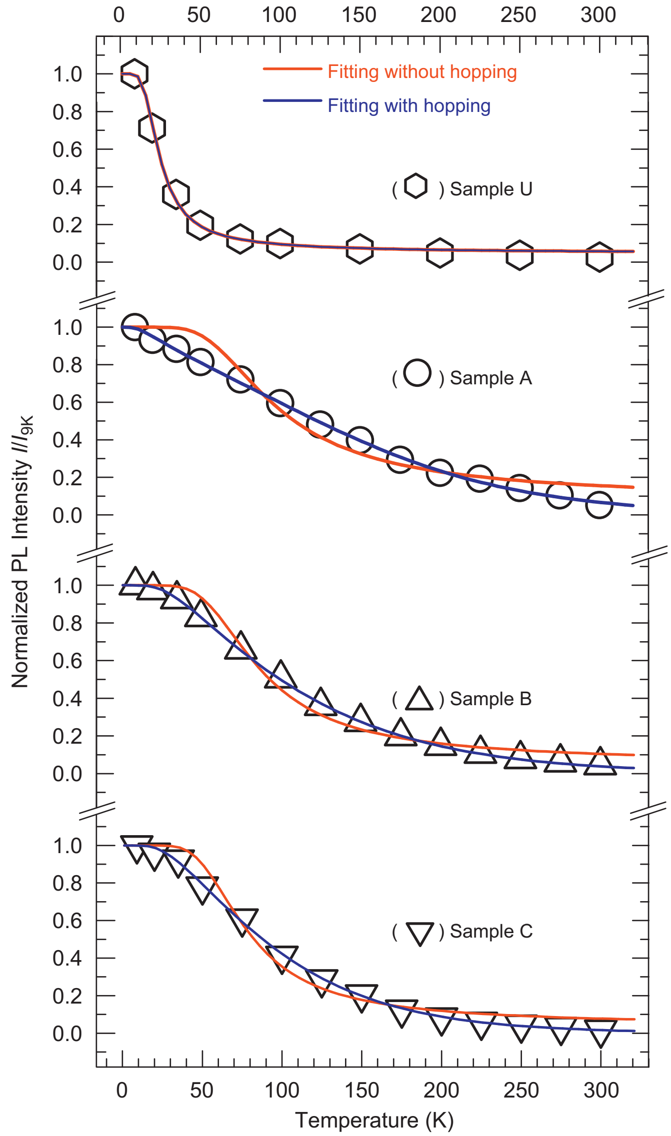

Fig. 5. Temperature-dependent fitting of the integral PL peak intensities in *wz*–CdZnO sample A, *wzrs*–CdZnO sample B, *rs*–CdZnO sample C, and ZnO sample U. The red and blue lines represent the fitting curves excluding and including the hopping term, respectively. (For interpretation of the references to colour in the figure legend, the reader is referred to the web version of this article.)

where E_a is the activation energy in a thermal quenching process, I_0 the integral PL peak intensity at 0 K, which was approximately substituted by the integral PL peak intensity at 9 K here, k_B the Boltzmann constant, and c a fitting parameter. Using this relation, the integral PL peak intensity data from ZnO reference sample were well fitted. However, evident deviations between the fitting and experimental data were clearly observed in the CdZnO samples. By adding a hopping thermal quenching term "T/T_B" to Eq. (3), the fittings in CdZnO samples were significantly improved. The blue lines in Fig. 5 show the fitting results using the relation with the hopping term [24–27],

$$\frac{I(T)}{I_0} = \frac{1}{1+\upsilon\exp(-E_a/k_BT+T/T_B)} \tag{4}$$

where T_B is a characteristic temperature and υ a fitting parameter. In the ZnO sample U, no evident change is observed after adding the hopping term. However, significant improvements are found in both *wz*–CdZnO and *rs*–CdZnO samples, which is a sign for the hopping process in the CdZnO samples. These hopping processes could happen among the band tail states and/or between a band tail state and some nonradiative defect states in the CdZnO. The band tail states are formed due to alloying effect and Cd distribution nonuniformity in the CdZnO samples. Band tail states from Cd nonuniformity were also observed in time-resolved PL studies on relatively small-Cd-concentration CdZnO samples [13]. The fitting parameters from both relations are summarized in Table 3.

Table 3
Fitting parameters on the temperature dependence of the integral PL intensity in CdZnO and ZnO samples.

No.	$\frac{I(T)}{I_0} = \frac{1}{1+c\,exp(-E_a/k_BT)}$		$\frac{I(T)}{I_0} = \frac{1}{1+\upsilon\,exp(-E_a/k_BT+T/T_B)}$		
	E_a (meV)	c	E_a (meV)	T_B (K)	υ
U	7.05	21.6	7.05	1.39×10^5	21.5
A	24.9	14.2	3.14	71.7	0.240
B	25.0	22.5	8.13	77.4	0.709
C	24.2	30.2	7.44	62.7	0.655

4. Summary

In summary, temperature-dependent PL measurements were performed on large-Cd-concentration ($E_g<3.0$ eV) *wz*–CdZnO, *rs*–CdZnO, and *wzrs*–CdZnO samples grown by MBE. The temperature dependence of the bandgap change in CdZnO and ZnO samples was fitted by Varshni and B–E relations. The bandgap fitting parameters could be useful for estimating the thermal-induced emitting-light wavelength shift in future CdZnO optoelectronic devices. The temperature-dependent integral PL intensity was fitted. The fitting relation with hopping term fits the experimental data much better than the relation without hopping term in CdZnO samples but no evident difference in the ZnO reference sample is observed, indicating the hopping process in the CdZnO samples is possibly associated with the band tail states due to alloying effect and Cd distribution nonuniformity.

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