



# Thermal stability of CdZnO thin films grown by molecular-beam epitaxy

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## ABSTRACT

CdZnO thin films with near-band-edge (NBE) photoluminescence (PL) emission from 2.39 eV to 2.74 eV were grown by plasma-assisted molecular-beam epitaxy on *c*-plane sapphire substrates with 800 °C in situ annealing. CdZnO thin films evolve from pure wurtzite (*wz*) structure, to mixture of *wz* and rock-salt (*rs*) structures confirmed by X-ray diffraction studies. Rapid-thermo-annealing (RTA) was performed on in situ annealed CdZnO samples. Pure *wz* CdZnO shows insignificant NBE PL peak shift after RTA, while mixture structure CdZnO shows evident blue shifts due to phase change after annealing, indicating the *rs* phase CdZnO changes to *wz* phase CdZnO during RTA process.

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## 1. Introduction

ZnO attracts considerable attentions for ultra-violet/blue light emitting diodes and laser diodes (LDs) due to its direct bandgap of 3.3 eV and large exciton binding energy of 60 meV at room temperature. The bandgap of ZnO can be made smaller by alloying Cd into ZnO [1–6] for potential visible light emitting device applications, such as green LDs. The thermal stability of CdZnO is an important issue for future reliable device application [7,8]. Due to the different crystal structures between wurtzite (*wz*) ZnO and rock-salt (*rs*) CdO, phase separation from *wz* to *rs* tends to happen in CdZnO, especially when large amount of Cd is alloyed into ZnO [4,9,10]. However, phase segregation and thermal stability studies of CdZnO have seldom been reported so far, especially on how the optical properties change after annealing. Since in situ annealing is an indispensable process for dopant activation [11–14], while RTA under nitrogen ambient is normally used for device contact formation [15–18] for ZnO based materials, we studied and reported the rapid thermal annealing effect on

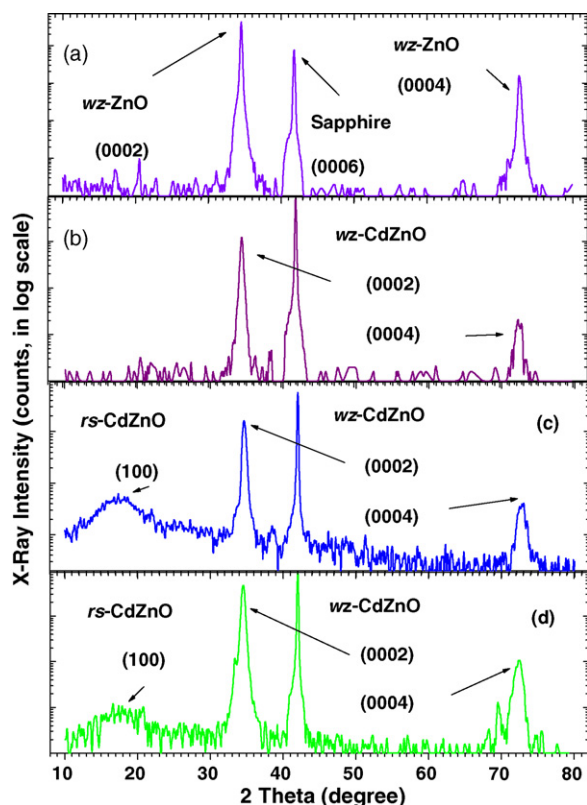
molecular-beam epitaxy (MBE) grown CdZnO thin films in this paper.

## 2. Experiment

CdZnO thin films were grown by plasma-assisted MBE on *c*-plane sapphire substrates. Elemental Zn (6N) and Cd (6N) heated by effusion cells were used as zinc and cadmium sources. Oxygen (5N) plasma generated by a radiofrequency plasma generator was used as the oxygen source. The samples were grown at very low growth temperatures (below 200 °C) to achieve large Cd incorporation. A thin ZnO buffer layer (10–20 nm) was first grown on substrate before CdZnO growth for each sample. These CdZnO samples were in situ vacuum-annealed in the chamber at 800 °C for 5 min after growth. Cd composition was controlled by tuning the ratio of Zn and Cd flux. Cd composition was measured by energy-dispersive X-ray spectroscopy (EDS). Room temperature (RT) PL measurements were carried out using a home-built PL system, with a 325-nm He–Cd laser as excitation source and a photomultiplier tube behind the monochromator as detector. RTA was then carried out at 800 °C in nitrogen ambient for 1 min on the CdZnO samples. X-ray diffraction (XRD) was performed in  $\theta$ – $2\theta$  geometry with a 0.1° resolution. To avoid the possible effect of non-uniformity of the

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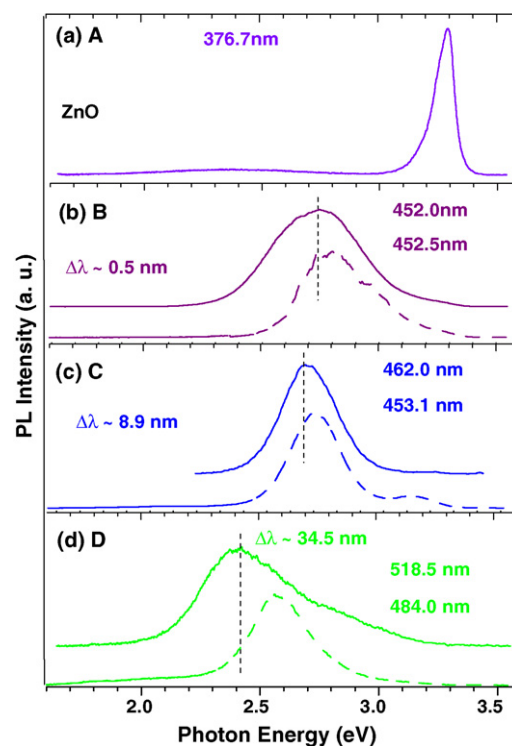


**Fig. 1.** XRD patterns of ZnO sample A (a) and CdZnO samples B–D [(b)–(d)]. The CdZnO samples evolve from pure wurtzite structure (B) to mixture of wurtzite and rock-salt structures (C and D) with increasing Cd composition.

samples on the spectra, PL and XRD measurements of the samples before and after RTA were carried out on less than 5 mm × 5 mm area of each sample.

### 3. Results and discussions

Fig. 1(a) and (b)–(d) show the XRD patterns of undoped ZnO sample A, and CdZnO samples B–D respectively. Samples A and B show only wz-ZnO/wz-CdZnO (0002) and (0004) peaks at  $2\theta = 34.5^\circ$  and  $72.5^\circ$  as shown in Fig. 1(a) and (b), indicating the pure wz structure. As Cd concentration is increased monotonously, samples C and D become mixture of wz and rs structures as shown in Fig. 1(c) and (d). Besides the wz-CdZnO (0002) and (0004) peaks, a broad rs-CdZnO (100) peak [19,20] at  $2\theta = 17.5^\circ$  is also observed, indicating the emergence of phase segregation in samples C and D, although the wz structure still dominates as sharper peaks. The intensity of rs-CdZnO (100) peak does not show significant change with increasing Cd concentration. The broad rs-CdZnO (100) peak is possibly due to the very low crystallinity of the rs phase in the CdZnO samples. In the XRD patterns, substrate signals of sapphire (0006) peaks at  $2\theta = 42.0^\circ$  are shown in all samples A–D. The crystal structures of the samples are summarized in Table 1. The Cd con-



**Fig. 2.** Room-temperature PL spectra before (solid lines) and after (dashed lines) RTA of CdZnO samples B–D in (b)–(d). The upper and lower wavelength values in (b)–(d) show the RT PL peak positions before and after RTA. The blue shift values are shown as  $\Delta\lambda$ . Room-temperature PL spectra of ZnO sample are shown in (a) as reference.

centrations ( $x$ ) of  $\text{Cd}_x\text{Zn}_{1-x}\text{O}$  samples B–D are also listed in Table 1, which show 0.05, 0.08 and 0.13, respectively.

Samples B–D were subject to the following experiments to investigate the annealing effect on the CdZnO. Firstly, RT PL measurements were performed on the as-grown samples B–D [solid lines shown in Fig. 2(b)–(d)]. Table 1 summarizes the CdZnO samples B–D with RT NBE PL positions covering from 2.74 eV to 2.39 eV, corresponding from violet to green in the visible region. The room-temperature NBE PL energies are assumed to be the bandgap energies of each sample. Then, the CdZnO samples were rapid thermal annealed at  $800^\circ\text{C}$  for 1 min. Finally, the RT PLs were carried out on the annealed samples. The dashed lines in Fig. 2(b)–(d) show the RT PL spectra of CdZnO samples B–D after RTA. In pure wz-CdZnO sample B, the NBE RT PL peak position shifted from 452.0 nm (2.743 eV) to 452.5 nm (2.740 eV) after RTA as shown in Fig. 2(b). The blue shift is only 0.5 nm, which is comparable to the resolution of the PL measurements. However, the RT NBE PL peaks of the mixture structural CdZnO samples C and D shift from 462.0 nm (2.684 eV) to 453.1 nm (2.737 eV), and from 518.5 nm (2.392 eV) to 484.0 nm (2.562 eV) after RTA, respectively. The blue shifts of 8.9 and 34.5 nm are observed, respectively.

To find out the reason of bandgap change after RTA, secondary ion mass spectroscopy (SIMS), EDS and XRD were carried out on

**Table 1**  
Crystal structure, bandgap  $E_g$ , film thickness and Cd concentration  $x$  in the  $\text{Cd}_x\text{Zn}_{1-x}\text{O}$  samples.

Sample no.	Description	Crystal structure <sup>a</sup>	Bandgap $E_g^b$ (eV)	Thickness (nm)	Cd concentration $x$
A	ZnO	wz	3.29	260	0
B	CdZnO	wz	2.74	200	0.05
C	CdZnO	wz and rs	2.68	150	0.08
D	CdZnO	wz and rs	2.39	200	0.13

<sup>a</sup> wz and rs represent wurtzite and rock-salt structures, respectively.

<sup>b</sup> RT NBE PL peak positions of the samples before RTA are approximately used for  $E_g$  of the samples.

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