

P. MISRA<sup>1,✉</sup>  
P.K. SAHOO<sup>2</sup>  
P. TRIPATHI<sup>3</sup>  
V.N. KULKARNI<sup>2</sup>  
R.V. NANDEDKAR<sup>3</sup>  
L.M. KUKREJA<sup>1</sup>

## Sequential pulsed laser deposition of Cd<sub>x</sub>Zn<sub>1-x</sub>O alloy thin films for engineering ZnO band gap

<sup>1</sup> Thin Film Laboratory, Centre for Advanced Technology, Indore 452 013, India

<sup>2</sup> Department of Physics, Indian Institute of Technology, Kanpur 208 016, India

<sup>3</sup> Synchrotron Utilisation Division, Centre for Advanced Technology, Indore 452 013, India

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**ABSTRACT** Alloy thin films of Cd<sub>x</sub>Zn<sub>1-x</sub>O with different Cd concentrations were grown by sequential ablation of ZnO and CdO targets alternately, using a third-harmonic Q-switched Nd : YAG laser. The Cd concentration in the films, measured by Rutherford back scattering, was varied by controlling the ablation time of the CdO target relative to that of the ZnO. The films were found to be of a highly *c*-axis-oriented wurtzite phase with high crystalline quality, up to a Cd concentration of approximately 8%, beyond which CdO segregation occurred. The band gap of the Cd<sub>x</sub>Zn<sub>1-x</sub>O thin films was found to decrease monotonically from approximately 3.3 eV to approximately 2.9 eV with increasing *x* until the onset of CdO segregation.

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### 1 Introduction

Currently, there is immense interest in the band-gap engineering of ZnO owing to the worldwide quest in developing photonic devices in the UV-blue spectral region based on this material [1]. It is well known that ZnO is a rugged oxide semiconductor with a direct band gap of about 3.3 eV at room temperature (RT) and a large excitonic binding energy of 60 meV [2]. These characteristics make it a promising candidate for various optoelectronic devices such as UV-blue light-emitting diodes [3], laser diodes, solar blind UV photo detectors [4] and resonant tunneling devices [5]. For the realization of these devices, a crucial prerequisite is to tailor the ZnO band gap. The band gap engineering of ZnO is also important for the development of quantum well structures [6] and spintronic systems [7] based on ternary and quaternary alloys such as Zn<sub>1-x</sub>Mn<sub>x</sub>O, Zn<sub>1-x</sub>V<sub>x</sub>O and Zn<sub>1-x-y</sub>Cd<sub>x</sub>Mn<sub>y</sub>O etc. Moreover, by tailoring the band gap of ZnO into the

visible spectral region, it can be applied to transparent self-emitting display devices [8].

One of the ways to engineer the band gap of ZnO is to alloy it with other binary oxides such as MgO and CdO. Ohtomo et al. [9] and Sharma et al. [10] have reported earlier a study of the metastable alloying of MgO and ZnO to increase its band gap to approximately 4.1 eV at a Mg concentration of approximately 33% using the pulsed laser deposition (PLD) method and mixed targets of different MgO concentration. We have shown earlier that by varying the O<sub>2</sub> ambient pressure during the PLD growth one can also control the concentration of Mg in Mg<sub>x</sub>Zn<sub>1-x</sub>O alloy films [11]. To decrease the band gap of the intrinsic ZnO, single-phase thin films of Cd<sub>x</sub>Zn<sub>1-x</sub>O have been grown using CdO and ZnO mixed targets [12]. Due to the significantly higher vapor pressure of CdO compared to that of ZnO, the Cd concentration in the PLD grown films in this case was found to be around four times less than that in

the target. It is well known that while the lattice structure of ZnO is hexagonal wurtzite, that of CdO is rock salt and the normal thermodynamic solubility limit of CdO in ZnO is only about 2% [13]. However, PLD can enable a Cd concentration up to approximately 7% in the resulting metastable alloy films, as reported by [12]. Cd<sub>x</sub>Zn<sub>1-x</sub>O films have also been grown by MBE with concentrations of Cd up to 5% by Sakurai et al. [8].

Recently, M. Yan et al. [14] have used sequential ablation of two separate targets of CdO and SnO<sub>2</sub> to deposit alloy thin films without significantly destroying the rock salt structure of CdO. By varying total exposure time of the laser pulses on the SnO<sub>2</sub> target they could vary the Sn content up to about 11.4% in those films. We have adopted the same sequential ablation scheme to grow Cd<sub>x</sub>Zn<sub>1-x</sub>O alloy films using separate ZnO and CdO targets. The Cd concentration in these alloy films was controlled by varying the total ablation time of the CdO target relative to that of the ZnO. Using this method, we have successfully grown predominantly single-phase Cd<sub>x</sub>Zn<sub>1-x</sub>O films with Cd concentrations up to approximately 8% and have achieved a reduction in the ZnO band gap to approximately 2.9 eV. The results of this experimental study are presented and discussed in this communication.

### 2 Experimental

An in-house-developed multi-target pulsed laser deposition system was used to grow Cd<sub>x</sub>Zn<sub>1-x</sub>O alloy thin films on chemically cleaned single-crystal Al<sub>2</sub>O<sub>3</sub> (0001) substrates. De-

✉ Fax: +91-0731/488-300, E-mail: pmisra@cat.ernet.in

tails about this system have been described elsewhere [11]. In short, a third-harmonic Q-Switched Nd : YAG laser (Quantel) operating at 355 nm with a pulse repetition rate up to a maximum of 10 Hz and a pulse width of approximately 6 ns was used for ablation of the palletized and sintered CdO and ZnO targets placed side by side in the evacuated growth chamber. These targets were ablated alternately, with only one target being exposed to the laser beam at a time in a sequence. By controlling the total laser beam exposure time of the individual targets, films of different compositions were grown. The ablation time for ZnO was chosen to be approximately 8 s and CdO was ablated for different predefined times in the range of 1 to 6 s to obtain different concentrations in the films. Although longer ablation times of CdO, up to 12 s, were used in these experiments, segregation of the CdO beyond 6 s rendered these films non-consequential. The alternate ablation sequence of the said targets was repeated a number of times to grow a desired thickness of films. The laser fluence was kept at approximately  $4 \text{ J/cm}^2$  and the pulse repetition rate at 10 Hz to ablate the targets. At this fluence, an average film deposition rate was about  $2 \text{ \AA/s}$ . The growth chamber was evacuated to a base pressure of  $1 \times 10^{-7}$  Torr using a turbo molecular pump and during the film deposition  $6 \text{ N}$  purity oxygen was purged into the chamber through a leak valve. The  $\text{O}_2$  ambient pressure was maintained at  $1 \times 10^{-2}$  Torr, which was found to be adequate for growing the stoichiometric films. The film growth was carried out at a substrate temperature of approximately  $750^\circ\text{C}$  and was followed by a 15 min post-deposition annealing in similar conditions of ambient pressure and temperature to facilitate the alloying.

These films were characterized by a normal  $\theta$ - $2\theta$  X-ray diffraction (XRD) method (Figures not shown) using a Rigaku diffractometer, high-resolution XRD using a Phillips X'Pert-MRD system with a resolution of  $0.005^\circ$ , optical transmission spectroscopy using a Shimadzu UV-3101PC photospectrometer and scanning electron microscopy (SEM) using a Phillips XL 30 CP system. The concentration of Cd in the films and film thickness were

measured by Rutherford back scattering (RBS) spectrometry. For this, a collimated ion beam of  $^4\text{He}^+$  having a beam size of about 1 mm square at an energy of approximately 1.24 MeV was used. Carrier concentration and mobility in these films were measured at RT by the van der Paw method using a Keithley 236 source unit. Indium metal was used to make electrical contacts on the films. Subsequently the films were annealed in a vacuum of  $10^{-6}$  Torr at  $450^\circ\text{C}$  for 15 min.  $I$ - $V$  measurements confirmed that the contacts thus made were Ohmic at RT.

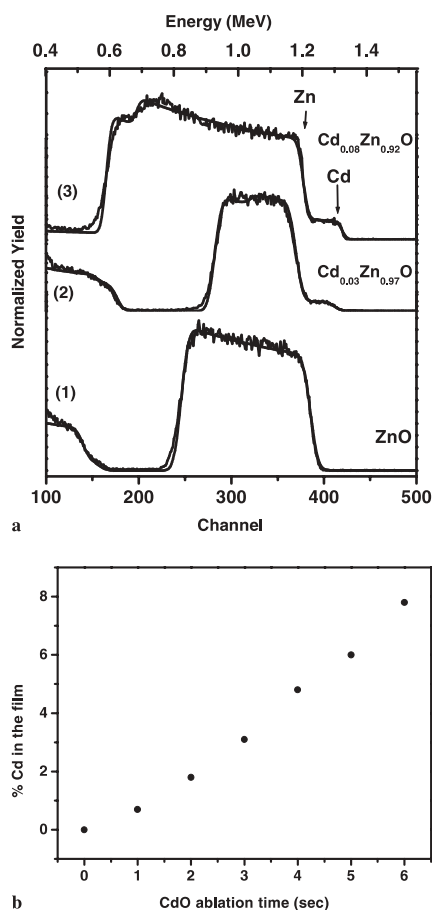
### 3 Results and discussion

Figure 1a shows the RBS spectra of the pure ZnO and alloy films with CdO ablation times of 3 and 6 s, while the ablation time of ZnO was kept constant at 8 s as mentioned earlier. Analyses of the RBS spectra were

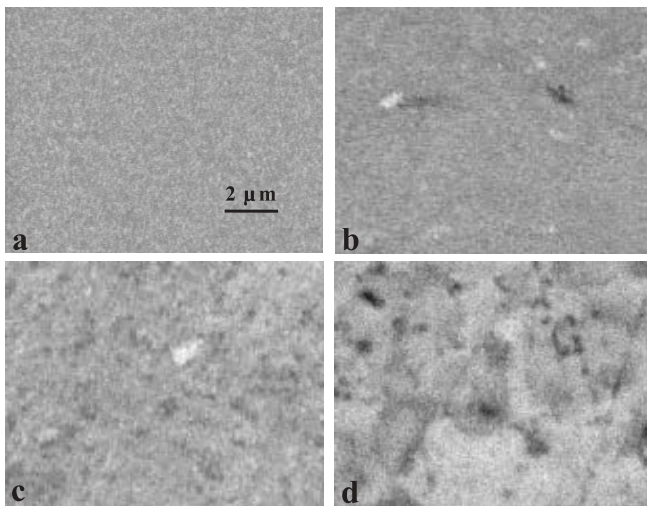
carried out using a software program called RUMP [15]. The composition and thickness of the films were determined by fitting the experimental spectra as shown in Fig. 3a by a smooth and continuous line. Spatial distribution of the Cd concentration was found to be nearly uniform throughout the film thickness up to a CdO ablation time of 6 s. For ablation times longer than this, the fitting of the RBS spectra showed random variation of Cd concentration in the films, which is expected to be due to the segregation of CdO in the films. Figure 1b shows the Cd concentration in single-phase  $\text{Cd}_x\text{Zn}_{1-x}\text{O}$  films of various thickness with different CdO ablation times up to 6 s.

Scanning electron micrographs of the  $\text{Cd}_x\text{Zn}_{1-x}\text{O}$  films with increasing Cd concentration, as measured by RBS, are shown in Fig. 2a-d. It can be seen in these micrographs that the film surface was smooth and free from particulates in all the cases. However, the surface degraded and the roughness increased with increasing Cd concentration up to approximately 8%, as can be seen in the micrographs from Fig. 2a to c. Above this concentration, as seen in the micrograph Fig. 2d, the film surface developed dark patches, which can perhaps be attributed to CdO segregation. The CdO segregation was also conspicuous in the HRXRD pattern for a Cd concentration of approximately 8%, as discussed in the following paragraph.

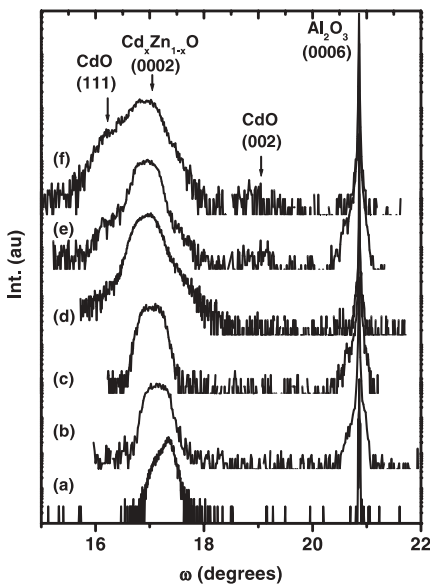
Figure 3 shows the high-resolution  $\omega$ - $2\theta$  XRD (HRXRD) patterns of the  $\text{Cd}_x\text{Zn}_{1-x}\text{O}$  thin films with different Cd concentrations. Films with Cd concentration  $< 8\%$  were found to be single phase and highly  $c$ -axis-oriented, exhibiting only (0001) peaks of the  $\text{Cd}_x\text{Zn}_{1-x}\text{O}$  alloy. The position of the (0002) peak of the  $\text{Cd}_x\text{Zn}_{1-x}\text{O}$  films was found to shift continuously towards smaller angles as the CdO concentration was increased from 0 to 8%, indicating an increase in the  $c$ -axis lattice parameter. The  $c$ -axis lengths calculated from HRXRD patterns are plotted as a function of Cd content in Fig. 4a. The  $c$ -axis parameter at a Cd concentration of approximately 8% was found to increase by approximately 1.5% as compared to that of the ZnO. The FWHM of the  $\omega$  rocking curve of the (0002) peak of the  $\text{Cd}_x\text{Zn}_{1-x}\text{O}$  films was found to increase monotonically from approxi-



**FIGURE 1** a Rutherford back scattering (RBS) spectra of ZnO (1) and  $\text{Cd}_x\text{Zn}_{1-x}\text{O}$  thin films with CdO ablation times of 3 s (2) and 6 s (3). b Cd concentration as a function of CdO ablation time in  $\text{Cd}_x\text{Zn}_{1-x}\text{O}$  thin films



**FIGURE 2** Scanning electron micrographs of  $\text{Cd}_x\text{Zn}_{1-x}\text{O}$  thin films with  $x$  approximately 0.03 (a),  $x$  approximately 0.06 (b),  $x$  approximately 0.08 (c) and  $x > 0.08$  (d)

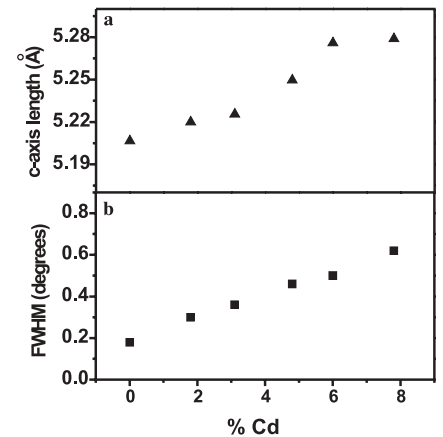


**FIGURE 3**  $\omega-2\theta$  scan of ZnO (a) and  $\text{Cd}_x\text{Zn}_{1-x}\text{O}$  thin films with  $x$  approximately 0.018 (b),  $x$  approximately 0.031 (c),  $x$  approximately 0.06 (d),  $x$  approximately 0.08 (e) and  $x > 0.08$  (f)

mately  $0.18$  to  $0.62^\circ$  with increasing Cd concentration from 0 to 8%, as shown in Fig. 4b. At the CdO concentration exceeding 8%, shoulders at  $\omega = 16.6$  and  $19.1^\circ$  were found to appear in the diffraction pattern, which grew in intensity with increasing CdO concentration. These humps have been found to correspond to the rock salt CdO (111) and CdO (002) impurity phases in wurtzite  $\text{Cd}_x\text{Zn}_{1-x}\text{O}$ . Since there is a regular trend in the broadening and shifting of the (0002) peak, and the rock salt CdO (111), CdO (002) peaks are almost non-existent in the HRXRD patterns at Cd concentrations below 8%, there is

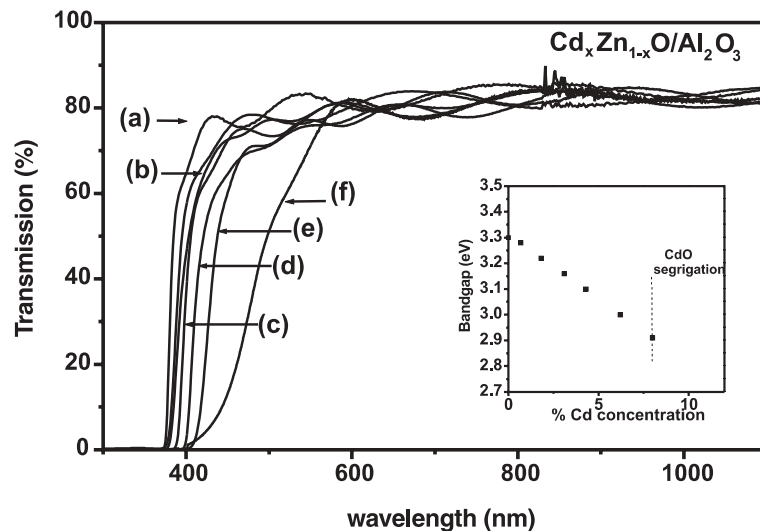
a strong reason to believe that the additional peaks emerging from the prime ones are due to the CdO segregation, which starts surfacing at a Cd concentration of approximately 8%, as can be seen in Fig. 3.

Figure 5 shows the optical transmission spectra of  $\text{Cd}_x\text{Zn}_{1-x}\text{O}$  thin films with different Cd concentrations. All the films were found to have a transmission exceeding 80% in the visible region, with typical spectral interference fringes. The absorption edge of the films shifted to red with increasing Cd concentration in the films, as can be clearly seen in this figure. The color of these films was found to change from



**FIGURE 4** Variation of the FWHM of the (0002)  $\text{Cd}_x\text{Zn}_{1-x}\text{O}$  peak (a) and  $c$ -axis lattice parameter (b) as a function of Cd concentration in the films

transparent to golden yellow with increasing Cd concentration. Similar observations on the color of the films have also been reported by Sakurai et al. in the  $\text{Cd}_x\text{Zn}_{1-x}\text{O}$  films grown by molecular beam epitaxy [8]. The band gap of these films was evaluated by plotting  $\alpha^2$  versus  $h\nu$  and extrapolating the linear portion of the curve to  $\alpha = 0$ . The inset of Fig. 5 shows the variation of the band gap of  $\text{Cd}_x\text{Zn}_{1-x}\text{O}$  thin films with varying Cd concentration. The band gap can be seen to decrease monotonically from approximately 3.28 to approximately 2.9 eV with Cd concentration increasing from 0 to approximately 8%. Above this concentration, the transmission spec-



**FIGURE 5** Optical transmission spectra of (a) ZnO and  $\text{Cd}_x\text{Zn}_{1-x}\text{O}$  thin films measured at room temperature with  $x$  approximately 0.018 (b),  $x$  approximately 0.031 (c),  $x$  approximately 0.06 (d),  $x$  approximately 0.08 (e) and  $x > 0.08$  (f). The inset shows variation of the band gap of  $\text{Cd}_x\text{Zn}_{1-x}\text{O}$  thin films with varying Cd concentrations below CdO segregation

tra showed an unusual behavior, as can be seen in Fig. 5, which could again be due to the segregation of CdO impurity phases in the  $\text{Cd}_x\text{Zn}_{1-x}\text{O}$  films.

The carrier concentration and carrier mobility, as measured by the van der Pauw method, did not have any systematic variation with respect to the Cd concentration. Rather, these were found to vary randomly in the ranges of approximately  $3 \times 10^{18}$  to  $6 \times 10^{19}$  /cc and  $8\text{--}16 \text{ cm}^2/\text{Vs}$ , respectively, for different films.

#### 4 Conclusions

In conclusion, we have grown highly oriented and single-wurtzite-phase  $\text{Cd}_x\text{Zn}_{1-x}\text{O}$  thin films with Cd concentrations up to approximately 8% using sequential ablation of CdO and ZnO targets alternately. All the films were found to be highly transparent in the visible region of the spectrum. The band gap of these films could thus be varied in the range from approximately 3.28 eV to approximately 2.9 eV by increasing the Cd concen-

tration. The carrier concentration and mobility were found to vary randomly in the ranges from approximately  $3 \times 10^{18}$  to  $6 \times 10^{19}$  /cc and  $8\text{--}16 \text{ cm}^2/\text{Vs}$ , respectively.

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