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Nonlinear optical properties of $Cd_xZn_{1-x}O$ films deposited with PLD technique

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ABSTRACT

In this paper, the structural and optical properties of $Cd_xZn_{1-x}O$ films were studied. The films were deposited with pulse laser deposition (PLD) technique. The Cd concentration changed in the range from $x=0$ to 0.2. The structure of the films was characterized by atom force microscope (AFM) and X-ray diffraction (XRD). The nonlinear optical properties were investigated by Z-scan methods. The two-photon absorption (TPA) coefficient β_{eff} was measured. The β_{eff} value changes from 49.2 cm/GW to 116.5 cm/GW with the Cd concentration from 0 to 15%.

1. Introduction

ZnO is a wide-gap semiconductor material, which has drawn a great interest for its excellent piezoelectric and optoelectronics. It can be developed into blue-green laser diodes and photonic devices. Up to now, many studies have been carried out such as photoluminescence (PL), room-temperature optical pumped ultraviolet laser emission, nonlinear optical properties etc. [1–5]. In the other hand, in order to adjust the band-gap of ZnO, the ternary alloy of doped ZnO was studied like $Mg_xZn_{1-x}O$, $Cd_xZn_{1-x}O$. It has been reported that the bandgap of ZnO could be widened up to ~4.0 eV by forming a ternary alloy of MgZnO [6]. On the other hand, the ionic radius Cd^{2+} (0.74 A) is close to that of Zn^{2+}. It is expected that alloyed $Cd_xZn_{1-x}O$ mixed crystal will expand the bandgap of ZnO. The lattice constants of $Cd_xZn_{1-x}O$ did not change significantly compared to those of ZnO. The band gap could be adjusted to 3.04 eV by incorporating Cd^{2+} with $x=0.20$ [7]. Besides the application of ZnO in ultraviolet photonic devices, the nonlinear optical properties are also attractive [8–10]. The second harmonic generation has been reported. Experiments show that ZnO has a large nonlinear second-order optical susceptibility $\chi^{(2)}$. Furthermore, the third-order nonlinear effect has been studied. The nonlinear refractive index γ, nonlinear absorption coefficient β were measured by Z-scan technique [11–14].

In this paper, we will report the nonlinear property researches of $Cd_xZn_{1-x}O$ films deposited with PLD technique. Cd concentration was changed from $x=0$ to $x=0.2$. The concentration dependent on the nonlinear optical coefficient was measured by Z-scan technique.

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2. Experiment

The $Cd_xZn_{1-x}O$ films were deposited on Al_2O_3 $(11\bar{2}0)$ substrates by PLD technique in an ultrahigh vacuum chamber. The targets were ablated by excimer laser pulses. The films were deposited at 450 °C in 5×10^{-5} Torr of pure oxygen. The cadmium content was determined by electron probe microanalyses. The substrates were degreased in organic solutions before being put into the growth chamber.

The crystallinity was characterized by a double crystal X-ray diffractometer (XRD) with CuKα radiation ($\lambda=1.5406$ Å) in 2θ-ω scan and ω scan modes (Philips X'pert MPD). The surface morphology was studied by AFM. Z-scan was carried out with a pulse laser at wavelength 780 nm, which was generated by a mode-locked Ti:Sapphire operating at a repetition rate 100 MHz with a pulse duration 100 fs. Open-aperture Z-scan was carried out. The sample was moved along the laser propagation. The laser was focused with a lens ($f=50$ cm). The beam waist was about 20 μm. Laser power was measured with a power meter (Newport 1835 C). PL signal was collected by a quartz lens ($f=30$ cm) then was redirected into spectrometer connected a CCD detector. The intensity of PL was measured by a photomultiplier (FACT50) tube and then averaged by an oscilloscope (Tektronix, TDS 3054 B).

3. Results and discussion

Fig. 1(a) shows the transmission spectra of the films at room temperature. As can be clearly seen, all of the films have high transmittance in the visible region. The edge of absorption moved to lower energy direction with the Cd content increased.

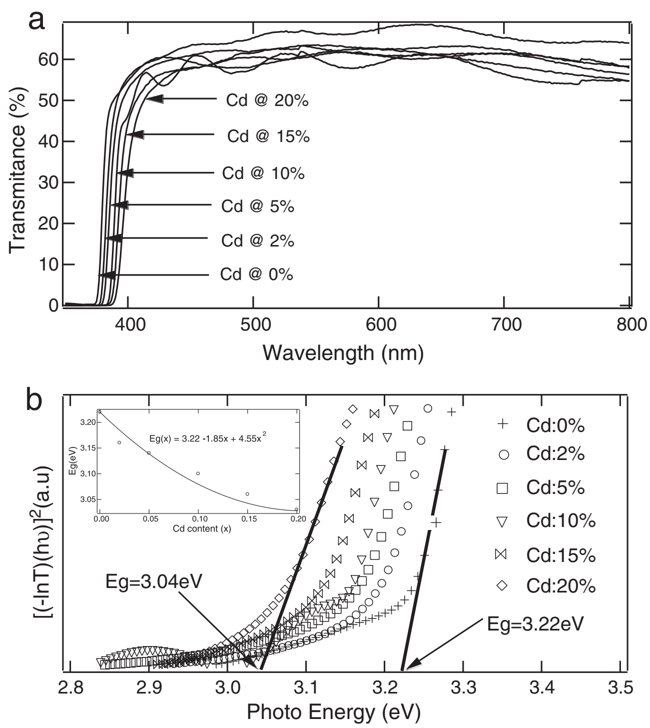

Fig. 1. (a) Room temperature transmission spectra of ZnO and$Cd_xZn_{1-x}O$ films, (b) dependence of the band gap energy of the ZnO and $Cd_xZn_{1-x}O$ films on the Cd content.

The absorption coefficient α can be calculated from the relation:

$$T = A\exp(-\alpha d) \tag{1}$$

where T is transmittance of the film, A is a constant, and d is the thickness of the film. That means α∝-(InT). The optical band gap E_g of the films is determined by applying the Tauc model. In the high absorption region:

$$\alpha h\nu = D\left(h\nu - E_g\right)^{1/2}. \tag{2}$$

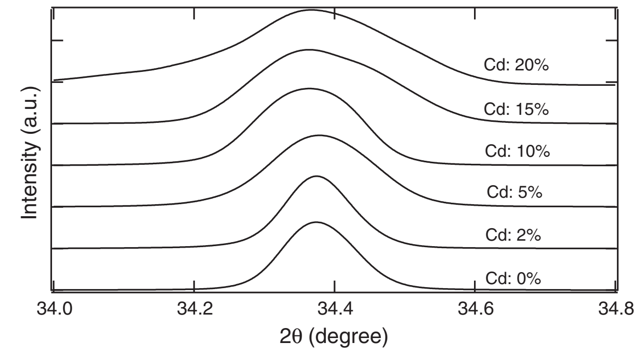

Fig. 3. XRD spectra of ZnO and $Cd_xZn_{1-x}O$ films with different Cd concentrations. The curves have been normalized for clarity.

Making a plot of $[(-\ln T)^*(h\upsilon)]^2$ versus the photon energy hυ by extrapolating the linear portion to the optical energy axis in the figure. The band gap E_g was estimated to be 3.22, 3.16, 3.14, 3.10, 3.06 and 3.04 eV for the films with the Cd contents of 0%, 2%, 5%, 10%, 15% and 20%, respectively. We could fit the x dependence of Eg values by a well-known equation in polynomial form, It could be written as $Eg\ (x) = 3.22 - 1.85x + 4.55x^2$. The results were inserted in Fig. 1(b). The band gap could be adjusted to 3.04 eV by incorporating Cd^{2+} with x = 0.20. This result is similar to the report of Makino etc. [15].

The surface morphology of the films was investigated by AFM images and shown in Fig. 2. The average grain size of the films is enlarged with increasing the Cd content.

The crystal structure, crystallite and lattice parameters of the films were studied. The result of XRD measurement for the different Cd contents ranging from 0 to 20% was shown in Fig. 3. The 2θ − ω scan data exhibited only (0 0 2) peaks for all of the films, which revealed that all of the films were single phase hexagonal wurtzite structure without any significant formation of a separated C_dO phase. From Fig. 3, we know that the peak positions were shifted to lower angles with the increasing of Cd content. That means the length of c-axis lattice constant of the films was increased with increasing Cd content. The theory indicates that c-axis can be expressed as

$$c = \frac{\lambda}{2\sin\theta}\sqrt{\frac{4}{3(a/c)^2}(h^2 + hk + k^2) + l^2} \tag{3}$$

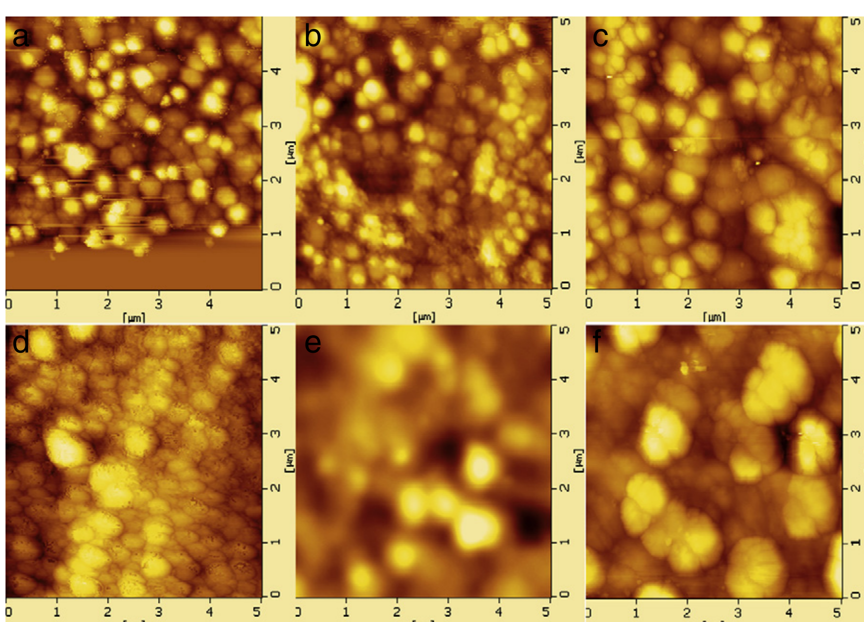

Fig. 2. AFM images of the surface morphology of ZnO and $Cd_xZn_{1-x}O$ films (a) ZnO, (b) $Cd_{0.02}Zn_{0.98}O$, (c) $Cd_{0.05}Zn_{0.95}O$, (d) $Cd_{0.10}Zn_{0.90}O$, (e) $Cd_{0.15}Zn_{0.85}O$, and (f) $Cd_{0.20}Zn_{0.80}O$.

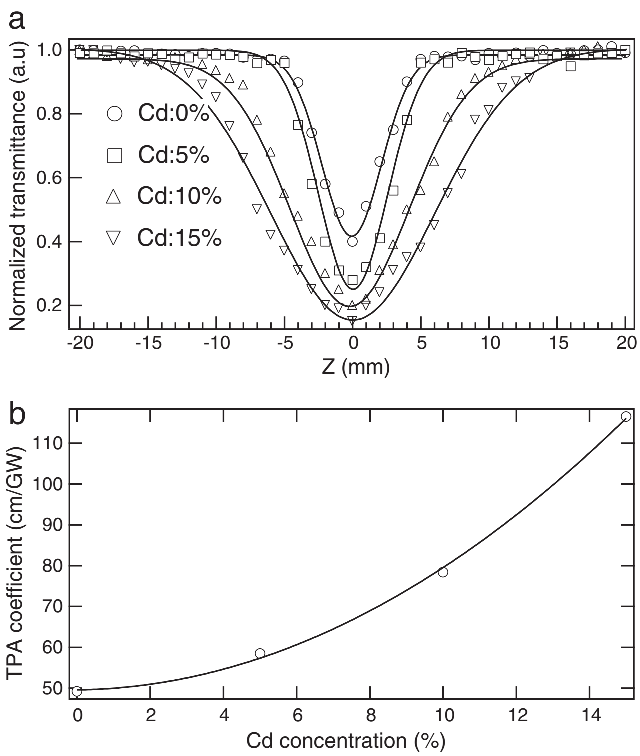

Fig. 4. (a) OA Z-scan measured with different Cd concentrations. (b) The plot of β_{eff} vs Cd concentrations.

where λ is the wavelength of X-ray and θ is the Bragg diffraction angle, hkl are Miller indices. The ratio of the c-axis of $Cd_{0.2}Zn_{0.8}O$ film and ZnO film is about 1.05. This result implies that no significant change happened in lattice constant when Zn^{2+} ion is replaced by Cd^{2+} ion because their ionic radius is similar. The value of full-widths at half-maximum (FWHM) for (0 0 2) diffraction peaks are 0.108 (x = 0), 0.110 (x = 0.02), 0.151 (x = 0.05), 0.159 (x = 0.10), 0.189 (x = 0.15) and 0.207 (x = 0.20). The small value of FWHM indicted that all of the films exhibit high crystalline quality.

The open-aperture Z-scan results were shown in Fig. 4(a). From the theory, the nonlinear absorption coefficient β_{eff} can be express as $q_0 = \beta_{eff} I_0 L_{eff}$, where L_{eff} is called effective thickness of the film and $I_0 = I_{00}/(1 + z^2/z_0^2)$. I_{00} is the intensity of laser beam at beam waist. Z is the distance from the focus point to sample. $Z_0 = \pi\omega_0^2/\lambda$ is the Rayleigh range. If the linear absorption coefficient is α, then $L_{eff} = [1\text{-}\exp(-\alpha L)]/\alpha$ where L is the thickness of the film. The normalized transmittance can be expressed as

$$T_{OA} = \sum_{m=0}^{\infty} (-1)^m \frac{q_0^m}{(m+1)^{3/2}}. \quad (4)$$

If $q_0 < 1$, higher order terms are ignored, the Eq. (2) can be expressed as

$$T_{OA} = 1 - {}_{eff} I_0 L_{eff}/2^{3/2}. \quad (5)$$

In our experiment, I_{00} was about 5GW/cm2, L was about 1 μm. The experiment can be fitting with Eq. (5)

Fig. 4(b) shows the value of β_{eff} as a function of Cd concentration. β_{eff} is increasing with the Cd concentration increased. From Fig. 2, the particle size of the samples becomes larger with the Cd concentration

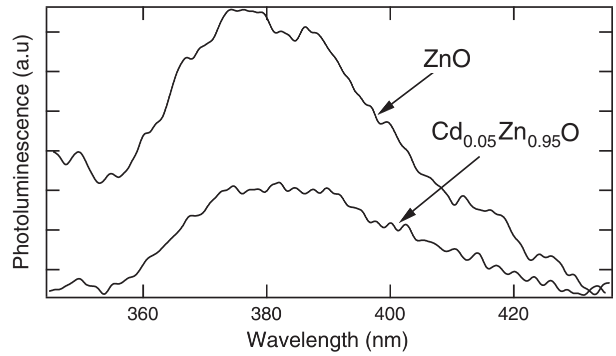

Fig. 5. PL spectra of the samples excited by 780 nm laser.

increased. That means β_{eff} increases with increasing particle size. The enhancement of nonlinear optical properties with increasing dimension originates from the size dependent enhancement of oscillator strength of coherently generated excitons.

Observed nonlinear absorption can be explained through two-photon absorption.

Using the samples of ZnO and $Cd_{0.05}Zn_{0.95}O$, we measure the photoluminescence (PL) of the sample excited by the 780 nm laser (100 fs, 100 Hz). Fig. 5 shows the experiment result. Comparing with the ZnO, the peak position of PL was shifted. This result was consistent with the transmission spectra.

4. Conclusion

In summary, the $Cd_xZn_{1-x}O$ films were deposited on Al_2O_3 $(11\bar{2}0)$ substrates with PLD technique. The nonlinear optical properties were investigated by Z-scan. The nonlinear absorption coefficient increases from 49.2 cm/GW to 116.5 cm/GW with the Cd concentration increasing from 0 to 15%. The enhancement of nonlinear optical properties with increasing dimension originates from the size dependent enhancement of oscillator strength of coherently.

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