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Effects of Mg doping concentration on the band gap of ZnO/$Mg_xZn_{1-x}O$ multilayer thin films prepared using pulsed laser deposition method

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Abstract Epitaxial ZnO/$Mg_xZn_{1-x}O$ multilayer thin films (x=0~0.15) were prepared on c-Al_2O_3 substrates by pulsed laser deposition and their crystallinity and optical properties were investigated using X-ray diffraction, TEM, and UV-Vis spectroscopy. ZnO/$Mg_xZn_{1-x}O$ multilayer thin films were grown by stacking alternate layers of ZnO and $Mg_xZn_{1-x}O$ with laser fluence of 3 J/cm^2, repetition rate of 5 Hz, substrate temperature of 600 °C, and oxygen partial pressure of 5×10^{-4} Torr. The thickness of individual ZnO and $Mg_xZn_{1-x}O$ layers was maintained at 3 and 6 nm, respectively, and the total thickness of the films was kept in 300 nm. X-ray diffraction results showed that the multilayer thin films were grown epitaxially on c-Al_2O_3 substrates with an epitaxial orientation relationship of $(0001)\left[10\bar{1}1\right]_{multilayer}\|(0001)\left[10\bar{1}1\right]_{Al_2O_3}$. Cross-sectional TEM micrographs showed alternating layers of bright and dark contrast, indicating the formation of ZnO/$Mg_xZn_{1-x}O$ multilayer thin films. The 2θ value of $Mg_xZn_{1-x}O$ (0002) peak increased from 34.30° at x=0 to 34.67° at x=0.15 with increasing Mg doping concentration in the multilayer thin films. The absorption edge in the UV-Vis spectra shifted to shorter wavelength from 360 at x=0 to 342 nm at x=0.15 and the band gap energy increased from 3.27 eV at x=0 to 3.54 eV at x=0.15.

Keywords ZnO · MgO · $Zn_xMg_{1-x}O$ · PLD · UV-detector · Multilayer

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1 Introduction

It has been well known that the ZnO based heterostructures are promising materials for applications in blue and ultraviolet light-emitting devices because of their excellent material properties of large exciton binding energy and band gap tenability [1–3]. Especially, magnesium oxide (MgO) is one of the strong candidate material for band gap engineering based on ZnO alloys. Because the crystal structure of MgO (cubic, a=0.424 nm) is quite different from that of ZnO (hexagonal, a=0.324 nm and c=0.520 nm), the solid solubility of MgO in ZnO is less than 4 mol% in the bulk form based on the phase diagram of the ZnO–MgO system [4]. However, similar ionic radii of Mg^{2+} (0.57 Å) and Zn^{2+} (0.60 Å) may alloy significant replacement each other during the metastable thin film fabrication process, and then results in high solid solubility of MgO in ZnO for the thin film alloys. There have been many reports on the growth of $Mg_xZn_{1-x}O$ thin films to control the band gap using various deposition techniques. Ohtomo et al. reported the growth of $Mg_{0.33}Zn_{0.67}O$ thin films using laser MBE [5], Choopun et al. reported the growth of MgZnO alloy films that have a band gap above 5.0 eV by the PLD [6], Liu et al. prepared $Mg_xZn_{1-x}O$ (x=0~0.15) nano-films using sol–gel method [7], and Kumar et al. prepared $Mg_xZn_{1-x}O$ (x=0~0.42) thin films using radio frequency sputtering method [8].

On the other hand, it has been well known that the artificial engineering of oxide and semiconductors for functional devices applications is possible by formation of multilayer thin films that show superior electrical and optical properties than the conventional single layer thin films [9, 10]. Zhang et al. reported the growth of ZnO/MgZnO single quantum wells in which the well width changes continuously grown by MOCVD [11], Wang et al. fabricated the ZnO/MgO multilayer thin films on Si (111)

by pulsed laser deposition, and Bhattacharya et al. reported the comparative study of Mg doped ZnO single layer film and multilayer ZnO/MgO thin films [12].

In this report, we have fabricated ZnO/$Mg_xZn_{1-x}O$ multilayer thin films on *c*-plane Al_2O_3 substrates by changing the Mg doping concentration (x=0, 0.05, 0.1, 0.15) as a method to control the band gap of the ZnO based alloy thin films. The effects of Mg doping concentration on the crystallinities and the optical properties of multilayer thin films have been investigated.

2 Experimental procedures

$Mg_xZn_{1-x}O$ thin films with different Mg concentrations were prepared on *c*-plane Al_2O_3 substrates using a multi-target PLD system equipped with a high-vacuum chamber up to 6×10^{-6} Torr. A KrF excimer laser was operated at a wavelength of 248 nm with the repetition rate of 5 Hz. *c*-plane Al_2O_3 substrates were ultrasonically cleaned in acetone, methanol, isopropyl alcohol, and deionized water sequentially. The cleaned substrate was loaded into the chamber and then heated to 600 °C at a base pressure of 6×10^{-6} Torr. ZnO and $Mg_xZn_{1-x}O$ (x=0, 0.05, 0.1, 0.15) targets, prepared by solid state sintering reaction of high-purity ZnO and MgO powders (Sigma-Aldrich, USA), were used to prepare both the single layer thin films (ZnO and $Mg_xZn_{1-x}O$) and the ZnO/$Mg_xZn_{1-x}O$ multilayer thin films. During the deposition process, the target-substrate distance was kept at 50 mm, the oxygen partial pressure was kept at ~5×10^{-4} Torr, and the energy density was of about 3 J/cm^2. The multilayer thin films, of which thickness was controlled by changing the deposition time, were successively prepared without breaking vacuum using the multi-target holders. The thicknesses of the individual ZnO layer and the $Mg_xZn_{1-x}O$ layer were kept with 3 nm/6 nm, respectively, and the total thickness of both the single layer thin films and the ZnO/$Mg_xZn_{1-x}O$ multilayer thin films was kept with 300 nm.

The phase of the thin films was characterized using X-ray diffraction (XRD; X'pert PRO, Philips, Eindhoven, Netherlands) operated at 40 kV and 40 mA. Microstructure, crystallographic orientation, and epitaxial nature of the films were analyzed using conventional transmission electron microscope (TEM) (JEM 2000EX, JEOL, Tokyo, Japan). Optical band gap was measured using UV-VIS spectroscopy (Cary 100, Varian, Mulgrave, Australia) at room temperature, in the range of 200–800 nm.

3 Results and discussions

Figures 1(a) and (b) show XRD $\theta-2\theta$ scans of ZnO/$Mg_xZn_{1-x}O$ (x=0~0.15) multilayer thin films grown on *c*-Al_2O_3 substrates and 2θ values of $Mg_xZn_{1-x}O$ (0002) peaks as a function of Mg doping concentration, respectively. Highly *c*-axis oriented $Mg_xZn_{1-x}O$ (0002) reflections corresponding to the hexagonal wurzite-phase are observed for all the films without any other peaks from the cubic MgO phase whose two strongest peak positions are marked with arrows in Fig. 1(a). This result of $\theta-2\theta$ scans shows that these multilayer films were grown in a single crystalline phase on *c*-Al_2O_3 substrates without any rock-

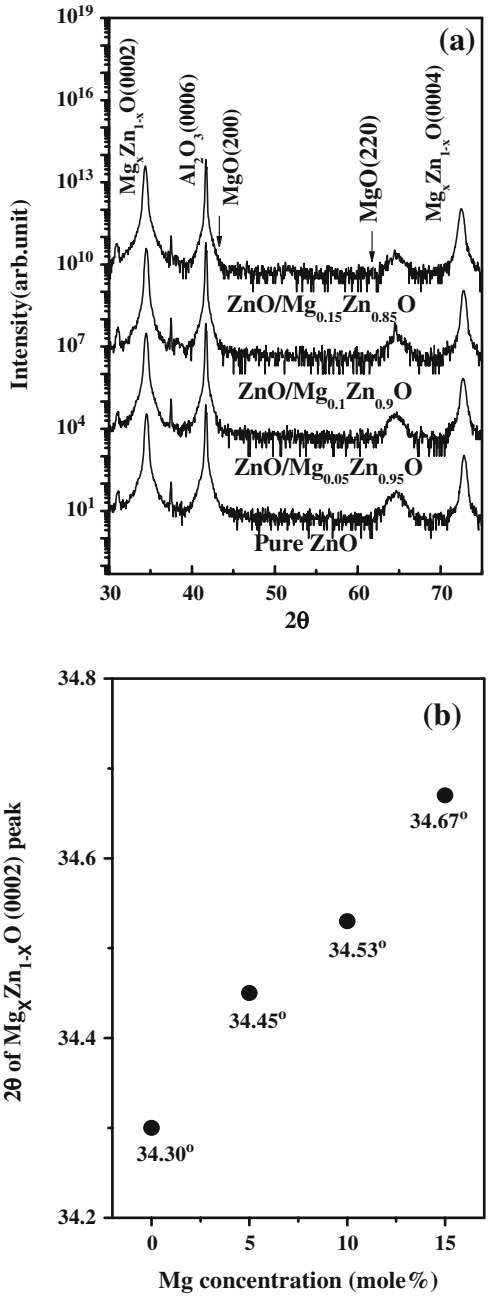

Fig. 1 X-ray diffraction $\theta-2\theta$ scans of the ZnO/$Mg_xZn_{1-x}O$ (x= 0~0.15) multilayer thin films grown on *c*-Al_2O_3 substrates using PLD method at 600°C and oxygen partial pressure of 5×10^{-4} Torr (**a**) and 2θ values of $Mg_xZn_{1-x}O$ (0002) peaks as a function of Mg doping concentration (**b**)

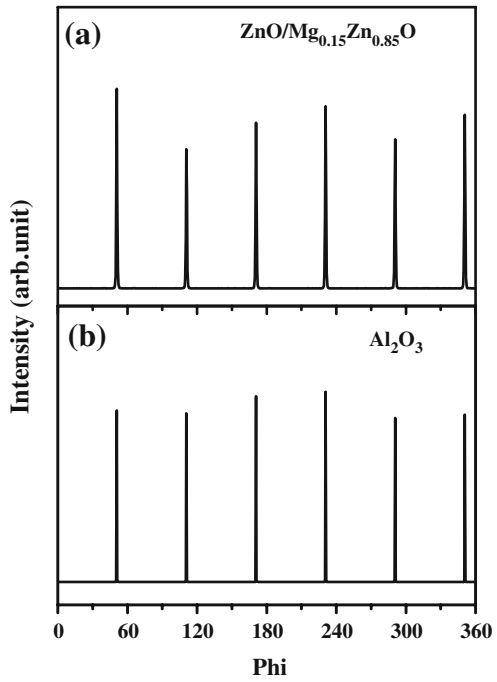

Fig. 2 XRD off-axis ϕ-scans of the $Mg_{0.15}Zn_{0.85}O\{10\bar{1}1\}$ planes (**a**) and $Al_2O_3\{10\bar{1}1\}$ planes (**b**), respectively, where the ZnO/$Mg_{0.15}Zn_{0.85}O$ multilayer thin films were grown on c-Al_2O_3 substrates using PLD method at 600°C and oxygen partial pressure of 5×10^{-4} Torr

salt cubic phase of MgO. It is also clearly observed in Fig. 1(b) that the $Mg_xZn_{1-x}O$ (0002) peaks shift systematically from lower angle (34.30°) toward higher angle (34.67°) with increasing Mg concentrations in the $Mg_xZn_{1-x}O$ layer from x=0 to x=0.15 [Fig. 1(b)]. The increase of diffraction angle of $Mg_xZn_{1-x}O$ (0002) peaks, i.e., the decrease of c-axis lattice constants with the increase in Mg concentrations is attributed to the relatively lower ionic radius of Mg^{2+}, which has been observed elsewhere by

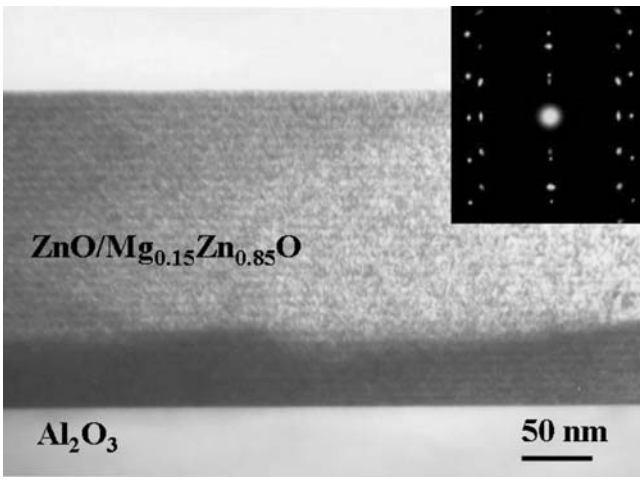

Fig. 3 Cross-sectional bright-field TEM micrograph of the $Mg_{0.15}Zn_{0.85}O$ multilayer thin film which were grown on c-Al_2O_3 substrates using PLD method at 600°C and oxygen partial pressure of 5×10^{-4} Torr. *Inset* is the corresponding selected area electron diffraction pattern obtained at the film/substrate interface

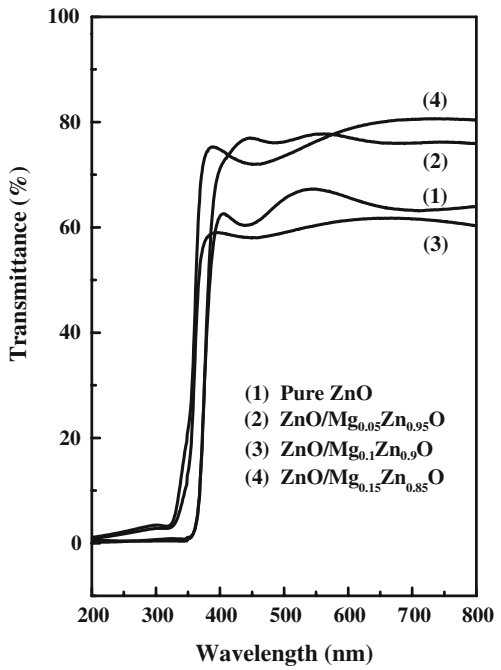

Fig. 4 Optical transmission spectra of the ZnO/$Mg_xZn_{1-x}O$ (x=0~x=0.15) multilayer thin films with various Mg doping concentrations measured at room temperature using UV-Vis spectrometer

many other researchers [12, 13]. In order to characterize in-plane epitaxy nature of multilayer films, off-axis XRD ϕ-scans were performed on $(ZnO/Mg_xZn_{1-x}O)_{multi\text{-}layers}$/$Al_2O_3$ specimens. Figures 2(a) and (b) show off-axis ϕ-scans of the $ZnO/Mg_{0.15}Zn_{0.85}O\{10\bar{1}1\}$ planes and $Al_2O_3\{10\bar{1}1\}$ planes, respectively. Peaks are only observed at every 60° at the same film/substrate ϕ-angle position indicating a good in-plane alignment between the film and

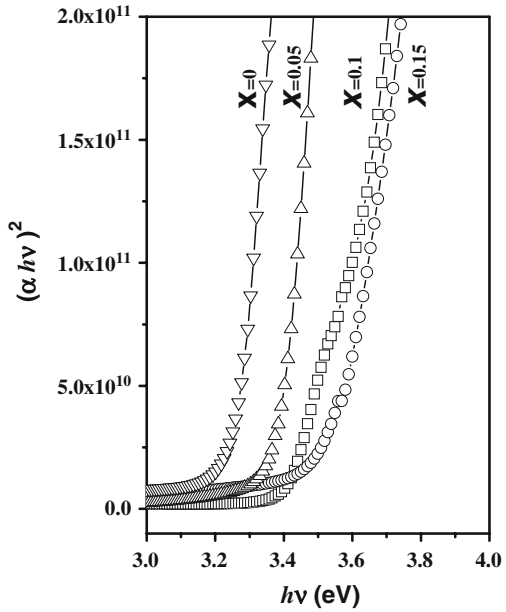

Fig. 5 Variation of $(\alpha h\nu)^2$ of the ZnO/$Mg_xZn_{1-x}O$ multilayer thin films as a function of photon energy ($h\nu$)

the substrate with hexagon on hexagon relationship. The XRD ϕ-scan results from all other specimens with different Mg doping concentration showed same in-plane orientation relationship as shown in Fig. 2. These XRD $\theta-2\theta$ and ϕ-scan results indicate that the ZnO/$Mg_xZn_{1-x}O$ multilayer thin films were grown epitaxially on c-Al_2O_3 substrates with epitaxial orientation relationship of $(0001)[10\bar{1}1]_{\text{multilayer}} \| (0001)[10\bar{1}1]_{Al_2O_3}$.

The microstructure and crystallinity of the ZnO/$Mg_xZn_{1-x}O$ multilayer thin films were also investigated using TEM. Figure 3 shows a typical cross-sectional bright-field TEM micrograph of the $Mg_{0.15}Zn_{0.85}O$ multilayer thin film. Inset is the corresponding selected area electron diffraction pattern (SADP) obtained at the film/substrate interface. It is clearly observed in the bright-field image that there are periodic alternating layers with bright and dark contrast in the film, which indicates that alternating ZnO/$Mg_{0.15}Zn_{0.85}O$ multilayer structure were successfully grown on c-Al_2O_3. This bright and dark contrast comes from the difference in the electron scattering factor between magnesium (Mg) and zinc (Zn). Indexing of the inset SADP shows the orientation relationship of $(0001)[10\bar{1}1]_{\text{multilayer}} \| (0001)[10\bar{1}1]_{Al_2O_3}$ between the film and the substrate. These TEM results are well consistent with the XRD results in Figs. 1 and 2.

Figure 4 shows the optical transmission spectra of the ZnO/$Mg_xZn_{1-x}O$ multilayer thin films with various Mg doping concentrations measured at room temperature using UV-Vis spectrometer. All the films show sharp absorption edges that shift toward shorter wavelength from 360 to 342 nm with increasing Mg doping concentration from x=0 to x=0.15. The band gap energy (E_g) of the multilayer thin film was calculated from the α^2 vs $h\nu$ plot by assuming that $\alpha^2 \propto (h\nu - E_g)$, where α is the absorption coefficient and $h\nu$ is the photon energy. The absorption coefficients (α) of the films were determined by using the following relation; $\alpha = [2.303 \times \log(1/T)]/d$ where T is the transmittance and d is the film thickness. Figure 5 shows $(\alpha h\nu)^2$ plots of the ZnO/$Mg_xZn_{1-x}O$ multilayer thin films as a function of photon energy. The band gap energies, obtained using the Fig. 5, of the multilayer thin films are 3.27, 3.37, 3.46, and 3.56 eV for the ZnO/$Mg_xZn_{1-x}O$ multilayer thin films with x=0, 0.05, 0.10, and 0.15, respectively. Even though the bandgap energies obtained in this study for pure ZnO and ZnO/$Mg_xZn_{1-x}O$ (x=0.05) are lower than the bulk ZnO value of 3.4 eV, the bandgap energies of ZnO/$Mg_xZn_{1-x}O$ multilayer thin films relatively increased with increasing Mg doping concentration x. This increasing band gap is attributed to the fact that MgO (E_g=7.8 eV) has a higher band gap than that of ZnO (E_g=3.4 eV). By increasing the doping concentration of MgO into ZnO, the effective band gap energy of the multilayer thin films increased in this study as reported by others. [3, 5] For the comparison, $Mg_xZn_{1-x}O$ (x=0.05~0.15) single layer thin films were also prepared in this study and then optical transmission spectra of the films were measured (not shown here). The band gap energies of those films were calculated to be 3.54, 3.60, 3.68 eV for x=0.05, 0.1, 0.15, respectively, which are larger than the corresponding multilayer thin films. These are similar values compare to the reported values of 3.5 and 3.8 eV for x=0.1 and 0.2 respectively, by Bhattacharya et al. [12]. From these results, it can be said that the band gap of Mg–ZnO alloy can be controlled by making ZnO/$Mg_xZn_{1-x}O$ multilayer thin films and by changing both the Mg doping concentration and the thicknesses of alternating ZnO/$Mg_xZn_{1-x}O$ layers.

4 Conclusions

We have fabricated epitaxial ZnO/$Mg_xZn_{1-x}O$ multilayer thin films (x=0, 0.05, 0.1, 0.15) by stacking alternate layers of ZnO and $Mg_xZn_{1-x}O$ on c-Al_2O_3 substrates and then controlled the band gap of the multilayer thin films by changing the Mg doping concentration. ZnO/$Mg_xZn_{1-x}O$ multilayer thin films have an epitaxial orientation relationship of $(0001)[10\bar{1}1]_{\text{multilayer}} \| (0001)[10\bar{1}1]_{Al_2O_3}$. As increasing Mg content in the multilayer thin films, the 2θ value of $Mg_xZn_{1-x}O$ (0002) peak increased from 34.30° at x=0 to 34.67° at x=0.15. The absorption edge in the UV-Vis spectra shifted to shorter wavelength from 360 at x=0 to 342 nm at x=0.15 and the band gaps of the multilayer thin films increased from 3.27 eV at x=0 to 3.54 eV at x=0.15. More work is in progress to control the band gap more systematically by changing both the thickness of the alternate layers and the Mg doping concentrations.

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