

# A Study of the Growth of Single-Phase $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{O}$ Films for UV LED

Hong Seung Kim, Chang Hoi Kim, Lili Yue

**Abstract**—Single-phase, high band gap energy  $\text{Zn}_{0.5}\text{Mg}_{0.5}\text{O}$  films were grown under oxygen pressure, using pulse laser deposition with a  $\text{Zn}_{0.5}\text{Mg}_{0.5}\text{O}$  target. Structural characterization studies revealed that the crystal structures of the  $\text{Zn}_{1-x}\text{Mg}_x\text{O}$  films could be controlled via changes in the oxygen pressure. TEM analysis showed that the thickness of the deposited  $\text{Zn}_{1-x}\text{Mg}_x\text{O}$  thin films was 50–75 nm. As the oxygen pressure increased, we found that one axis of the crystals did not show a very significant increase in the crystallization compared with that observed at low oxygen pressure. The X-ray diffraction peak intensity for the hexagonal-ZnMgO (002) plane increased relative to that for the cubic-ZnMgO (111) plane. The corresponding c-axis of the h-ZnMgO lattice constant increased from 5.141 to 5.148 Å, and the a-axis of the c-ZnMgO lattice constant decreased from 4.255 to 4.250 Å. EDX analysis showed that the Mg content in the mixed-phase ZnMgO films decreased significantly, from 54.25 to 46.96 at.%. As the oxygen pressure was increased from 100 to 150 mTorr, the absorption edge red-shifted from 3.96 to 3.81 eV; however, a film grown at the highest oxygen pressure tested here (200 mTorr).

**Keywords**—MgO, UV LED, ZnMgO, ZnO.

## I. INTRODUCTION

ZNO-BASED oxide semiconductors have attracted considerable attention as promising candidates for optical and electronic device applications, because they display a large exciton binding energy of 60 meV at room temperature, and have a wide band gap (3.37 eV) [1], [2]. Improving the stability of the excitons in ZnO could enable the preparation of highly efficient optoelectronic devices. The emission and absorption spectra of semiconductors can be tuned by alloying with a variety of materials [3]. For example, band gap engineering in ZnO can be performed by alloying with MgO, and the band gap energy of a ternary  $\text{Zn}_{1-x}\text{Mg}_x\text{O}$  alloy can be tuned from 3.37 to 7.8 eV by varying the Mg content from 0% to 100% [4]. Because the ionic radius of  $\text{Mg}^{2+}$  (0.57 Å) is close to that of  $\text{Zn}^{2+}$  (0.6 Å), ternary  $\text{Zn}_{1-x}\text{Mg}_x\text{O}$  alloy thin films, which are prepared by substituting  $\text{Mg}^{2+}$  for  $\text{Zn}^{2+}$  ions in the ZnO lattice, are suitable as potential barrier materials. During alloying, a degree of ion substitution can be tolerated in both the ZnO and MgO structures without changing the original structure; however, large crystals of ZnO and MgO are stabilized within wurtzite and rocksalt structures, respectively. Therefore, differences between the ZnO and MgO crystalline structures will result in

phase separation at certain composition ratios, which can cause unstable phase mixing [5]. The structural transition from a hexagonal wurtzite to a cubic structure could limit the utility of a  $\text{Zn}_{1-x}\text{Mg}_x\text{O}$  alloy near mixed-phase regions. Ohtomo et al. [6] reported the solid solubility of MgO in ZnO to be 33 mol% for a thin film alloy grown under metastable conditions. Above 33%, MgO was reported to segregate from the wurtzite ZnMgO lattice, limiting its maximum band gap to 3.9 eV.

Experimentally, this solubility limit can vary widely, and depends on the growth conditions and techniques used during preparation. Metastable  $\text{Zn}_{1-x}\text{Mg}_x\text{O}$  films with low Mg contents ( $x \leq 0.33$ ) and a hexagonal phase (a ZnO-like wurtzite structure), or high Mg contents ( $x \geq 0.51$ ) and a cubic phase (a MgO-like NaCl structure) have been grown using various techniques, including pulsed laser deposition (PLD) [7], metal organic chemical vapor deposition (MOCVD) [8], [9], RF co-sputtering [10], and molecular beam epitaxy (MBE) [11]. Among the various methods used for the epitaxial growth of ZnO films, PLD is attractive because it can deposit a film with a composition ratio close to that of the target. In the PLD process, the deposition oxygen pressure is a crucial parameter in ensuring the growth of high-quality, high Mg-content ZnMgO. Only a few studies have reported the effects of these growth conditions on the structural and optical band gap energy properties of ZnMgO thin films grown using high Mg-content targets.

In this study, we investigated the influence of the PLD conditions, including the oxygen pressure, on the structure of the prepared thin films. We fabricated ZnMgO thin films with  $x = 0.46$ – $0.54$  at.%, using a single  $\text{Zn}_{0.5}\text{Mg}_{0.5}\text{O}$  target, and we compared the structural and optical band gap energy properties of the prepared films.

## II. EXPERIMENT

$\text{Zn}_{0.5}\text{Mg}_{0.5}\text{O}$  thin films were grown on 0.43-mm-thick c-sapphire substrates, in a PLD system. Prior to the deposition of the  $\text{Zn}_{0.5}\text{Mg}_{0.5}\text{O}$  thin films, the c-plane sapphire substrates were cleaned by washing in organic solvents; this consisted of ultrasonication in acetone for 5 min, ultrasonication in methanol for 5 min, dipping in a buffered oxide etching (BOE) solution for 1 min, washing in DI water, and drying under a nitrogen flow. A KrF excimer laser with  $\lambda=248$  nm was used; the duration of the laser pulse was 25 ns, the laser energy was 200 mJ, and the pulse frequency was 3 Hz. The growth rate was 0.42 Å/s, and the distance between the  $\text{Mg}_{0.5}\text{Zn}_{0.5}\text{O}$  target and the substrate was maintained at 4.5 cm during film deposition. Using a turbo pump, the chamber was evacuated to give a pressure of  $3 \times 10^{-6}$  Torr. During the growth procedure, the

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temperature was maintained at 400°C, and the oxygen pressure was held constant at different values between 100 and 200 mTorr (with the different values used in different experiments).

The crystal structures of the  $Zn_{1-x}Mg_xO$  films were investigated using X-ray diffraction (XRD) and transmission electron microscopy (TEM). The composition states of all films were characterized using energy dispersive X-ray (EDX) analysis. The bandgap energy properties were investigated using UV-visible spectroscopy (UV).

### III. RESULTS AND DISCUSSION

The effects of the oxygen pressure on the structural properties of  $Zn_{1-x}Mg_xO$  thin films were investigated by depositing  $Zn_{1-x}Mg_xO$  thin films at a fixed substrate temperature of 400°C, while the oxygen pressure was varied from 100 to 200 mTorr. We note that a low growth temperature was favorable for the growth of high Mg-content, single-phase, hexagonal wurtzite ZnMgO (h-ZnMgO) thin films [7].

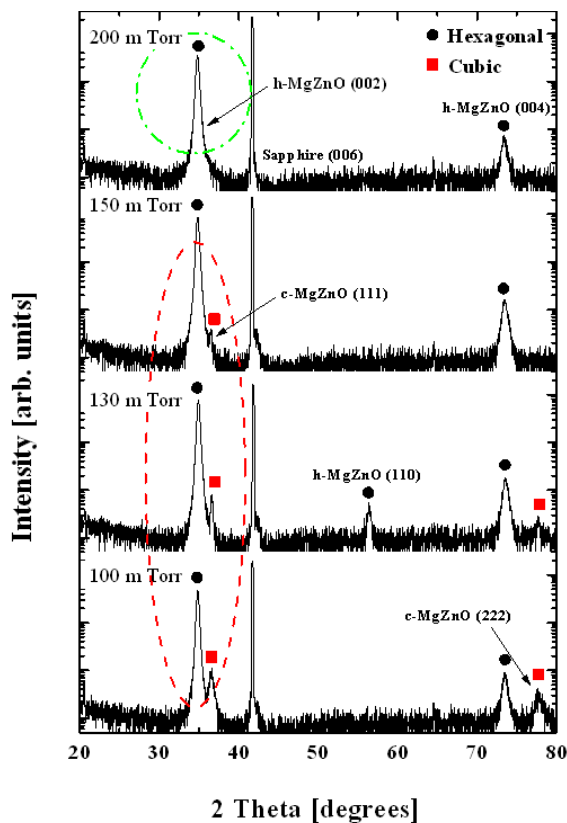


Fig. 1 X-ray diffraction patterns for  $Zn_{1-x}Mg_xO$  thin films grown at different oxygen pressures

Fig. 1 shows XRD patterns for the  $Zn_{1-x}Mg_xO$  thin films created using various PLD oxygen pressures. A phase evolution from mixed to hexagonal was evidenced in the XRD peak intensities. An oxygen pressure of 100 mTorr yielded both h-ZnMgO (002) and cubic-ZnMgO (c-ZnMgO) (111) diffraction peaks. The appearance of these structures suggested that cubic ZnMgO with low Zn contents had begun to precipitate as a secondary phase. Films grown at 100–150

mTorr displayed a (111) diffraction peak that weakened in intensity at higher oxygen pressures. This indicated that a mixed-phase structure, rather than a cubic phase structure, was present in the ZnO state. Interestingly, an oxygen pressure of 200 mTorr produced only a (002) diffraction peak, indicating that the resulting ZnMgO films were single-phase wurtzite structures. This showed that the high Mg-content  $Zn_{0.5}Mg_{0.5}O$  films had single-phase hexagonal wurtzite structures at certain oxygen pressures.

The lattice constants of the samples were calculated according to the following equations: h-ZnMgO (002) peak  $2\theta$  values,  $a=c/1.633$ ,  $\lambda=2d\sin\theta$ , and  $2d=c$ ; c-ZnMgO (111) peak  $2\theta$  values,  $a = \lambda/2 \sin\theta \sqrt{h^2 + hk + k^2}$ , where  $a$  is the lattice constant,  $h$ ,  $k$ , and  $l$  are Miller indices, and  $\lambda$  and  $\theta$  are the X-ray wavelength ( $\lambda = 1.5418 \text{ \AA}$ ) and the Bragg angle, respectively.

Fig. 2 shows the lattice constants of the (002) and (111) peaks for  $Zn_{1-x}Mg_xO$  films grown at different oxygen pressures. Increasing the oxygen pressure from 100 to 150 mTorr resulted in a reduction in all of the corresponding  $a$ -axes of the c-ZnMgO lattice constants from 4.255 to 4.250 Å. This indicated that the lattice constant of ZnMgO was highly dependent on the Mg content. As the oxygen pressure was increased from 100 to 200 mTorr, the  $c$ -axis of the h-ZnMgO lattice constant increased from 5.141 to 5.148 Å. These values were smaller than the  $c$ -axis lattice constant of pure ZnO (5.204 Å). This was due to the smaller ionic radius of  $Mg^{2+}$  (0.57 Å) compared with that of  $Zn^{2+}$  (0.6 Å). It was estimated that the Mg contents were more than 50 at.%, in contrast with the results reported by Chen et al. [12] and Kaushal et al. [13]. This result was confirmed in the EDX measurement results.

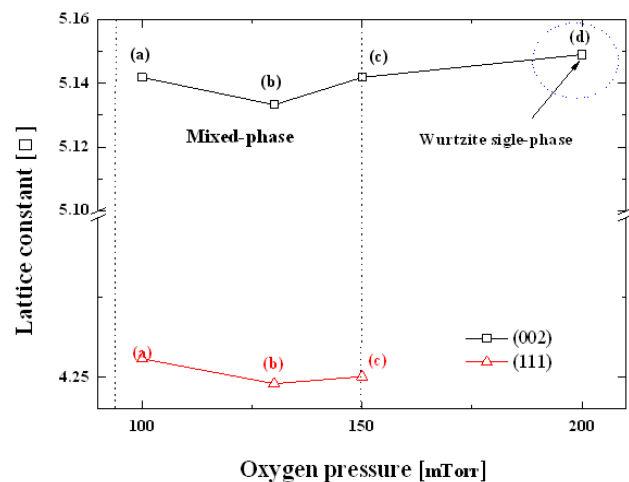


Fig. 2 Lattice constants for  $Zn_{1-x}Mg_xO$  (002) and (111) peaks grown at different oxygen pressures. (a) 100, (b) 130, (c) 150, and (d) 200 mTorr

Fig. 3 shows the EDX spectra for a  $Zn_{0.53}Mg_{0.47}O$  thin film deposited at an oxygen pressure of 200 mTorr. The main peaks corresponding to OK, ZnL, and MgK (which were incorporated in the film) were observed at 0.53, 1.01, and 1.25 keV, respectively. This result clearly indicated the incorporation of Mg into the ZnO layer. The EDX spectra displayed minor peaks

corresponding to ZnK at 8.68 keV, and a strong Al element peak was present at 1.19 keV, corresponding to the sapphire substrate signal.

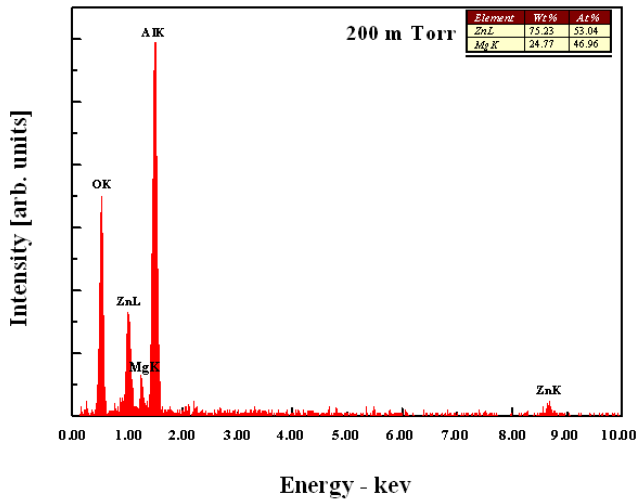


Fig. 3 EDX spectra for  $Zn_{1-x}Mg_xO$  grown at an oxygen pressure of 200 mTorr

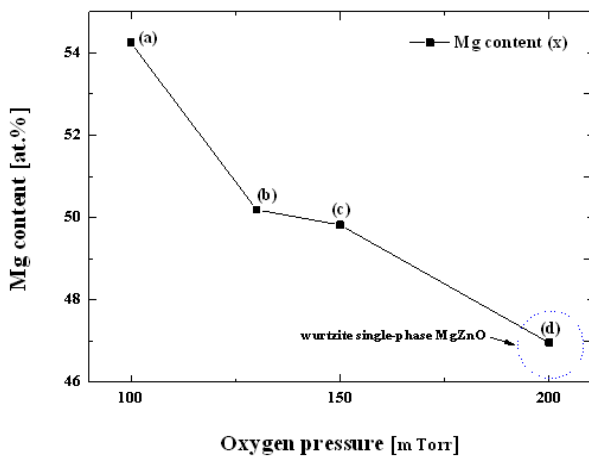


Fig. 4 Oxygen pressure dependence of the Mg content in the  $Zn_{1-x}Mg_xO$  thin films. (a) 100, (b) 130, (c) 150, and (d) 200 mTorr

As shown in Fig. 4, EDX analysis revealed that as the oxygen pressure was increased from 100 to 200 mTorr, the Mg content in the  $Zn_{1-x}Mg_xO$  films decreased from 54.25 to 46.96 at%. The results for the ternary  $Zn_{1-x}Mg_xO$  thin films showed that as the oxygen pressure increased, the amount of oxygen in the films increased, and the distribution of Mg in the films decreased. This meant that if the oxygen pressure was not high enough when the thin films were deposited, more Mg-O than Zn-O combination occurred. This was because the Mg atom is more likely to lose an electron than the Zn atom, in accordance with Pauli's beta principle (Mg: 1.31, Zn: 1.65), and its activity level is higher. Accordingly, as the frequency of Zn-O combination increased (along with the frequency of Mg-O combination) at 200 mTorr (i.e., when there was sufficient oxygen pressure), the Zn-O content in the thin films increased; however, because the frequency of Mg-O combination was

much lower for pressures lower than 130 mTorr (i.e., when there was not enough oxygen pressure), the Zn-O content in the thin films decreased as the pressure decreased. In this case, the Mg content in the  $Zn_{1-x}Mg_xO$  films decreased. This result showed that as oxygen pressure increased, the Mg content decreased compared with the XRD diffraction pattern shown in Fig. 1, thereby increasing the lattice constant value.

It is known that the hexagonal wurtzite structure of ZnO is most stable when the coordination number is 12, while the cubic structure of MgO is most stable if the coordination number is 6. It can therefore be inferred that if enough oxygen is supplied to meet this requirement, the hexagonal wurtzite structure will be more stable and advantageous than the cubic structure. In addition, it was confirmed in these tests that when thin films of  $Zn_{1-x}Mg_xO$  were grown at low oxygen pressures, c-ZnMgO structures formed, or phase separation occurred, and when the thin films were grown with sufficient oxygen pressure (in this case, 200 mTorr), only an h-ZnMgO' single structure phase could be observed.

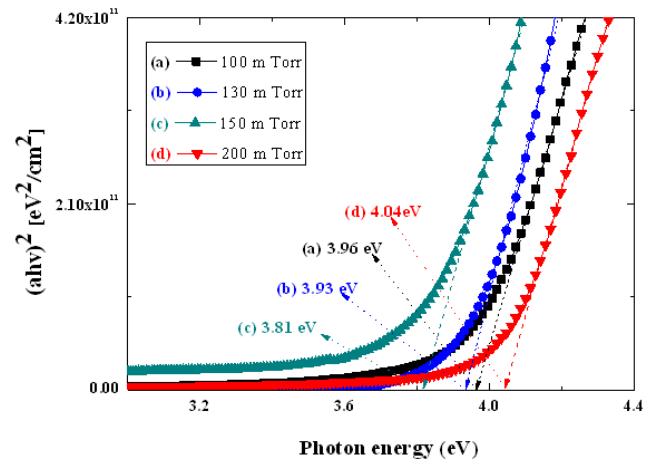


Fig. 5 Optical band gap energies of  $Zn_{1-x}Mg_xO$  thin films grown at oxygen pressures of (a) 100, (b) 130, (c) 150, and (d) 200 mTorr

Fig. 5 shows the optical band gap energy ( $E_g$ ) of the  $Zn_{1-x}Mg_xO$  thin films as a function of oxygen pressure, as measured using UV-vis spectrometry. The optical band gap energy ( $E_g$ ) was calculated from a plot of  $\alpha^2$  vs.  $E_g$ , assuming that  $\alpha^2 \propto (h\nu - E_g)$ , where  $\alpha$  is the absorption coefficient and  $h\nu$  is the photon energy. The films grown at 100–150 mTorr revealed a shift in the absorption edge to lower energies, from 3.96 to 3.81 eV. This was attributed to the lower Mg content in h-ZnMgO, which was caused by phase segregation. However, the ZnMgO films grown at 200 mTorr showed a wurtzite single-phase structure, with a higher energy of 4.04 eV. This result indicated that the crystal structure of the high Mg-content ZnMgO films was controlled by both the growth temperature and the oxygen pressure  $E_g$ .

Figs. 6 and 7 show cross-sectional bright-field TEM image of  $Zn_{1-x}Mg_xO/c$ -sapphire, near the interface and the corresponding SADP images for 100 and 200 mTorr, respectively. The SADP image in Fig. 6 can show that the diffraction spots from sapphire substrate denoted by underlined

index and rotated extra spots diffracted from ZnMgO film. We analyzed with the results of SADP and xray-diffraction pattern that the axis of the ZnMgO phase became in mix and the crystallinity of the thin films decreased. It was also due to defects between the two kinds of structure. The SAPD of the 200 mTorr in Fig. 7 did not appear the rotating extra spots. It was confirmed that the columns of ZnMgO films were denser and more uniform than those in Fig. 6. Also, crystallinity was much improved compared with low oxygen pressures by observing the diffraction pattern beam shape.

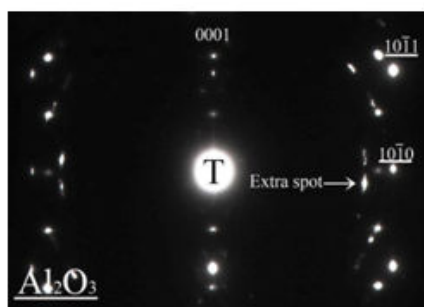


Fig. 6 Cross-sectional bright-field TEM image of  $Zn_{1-x}Mg_xO/c$ -sapphire near the interface and the corresponding SADP image for 100mTorr

#### IV. CONCLUSION

In summary, we fabricated single-phase wurtzite  $Zn_{1-x}Mg_xO$  thin films under various oxygen pressures, using the PLD technique. The crystal structures of the high Mg-content thin  $Zn_{1-x}Mg_xO$  films could be controlled by changing the oxygen pressure. The Mg content in the mixed-phase ZnMgO thin films could be modulated in the range from 54.25 to 49.82 at.% by controlling the oxygen pressure. Increasing the oxygen pressure to 200 mTorr resulted in the disappearance of the c-ZnMgO (111) peak, suggesting that the ZnMgO films were single-phase wurtzite in structure. Working from SADP images, we noted that other crystal axes did not appear, and that the crystallinity was much improved compared with that observed for other lowoxygen pressures; this was determined by observing the diffraction pattern beam shape. The single-phase wurtzite ZnMgO films displayed a band gap energy of 4.04 eV

and a c-axis lattice constant of 5.1418 Å, which was smaller than that of pure ZnO (5.204 Å). EDX analysis indicated that the Mg content in the ZnMgO film was 46.96 at.%.

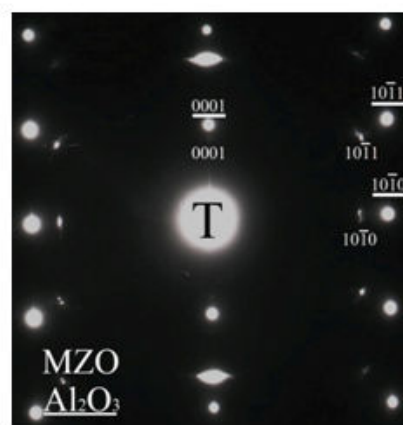


Fig. 7 Cross-sectional bright-field TEM image of  $Zn_{1-x}Mg_xO/c$ -sapphire near the interface and the corresponding SADP image for 200 mTorr

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