

## Preparation of zinc-doped magnesium oxide layer on a glass substrate by chemical solution deposition

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**Zn<sub>1-x</sub>Mg<sub>x</sub>O thin films on soda-lime-silica glass substrates were prepared by chemical solution deposition (CSD) using a metal naphthenate precursor. The films were obtained by a 5 cycle spin-coated technique and pre-fired as-deposited films followed by final annealing in air at 550 °C for 30 minute. High resolution X-ray diffraction was used to verify the crystal structure of the films. Films with up to 50 mol% Mg incorporation were more than 85% transparent in the visible spectra region and the absorption edge shifted to a shorter wavelength as the Mg content increased.**

**Key words:** ZnO, MgO, Thin film, Transmittance.

### Introduction

Recently, Ohtomo et al. proposed that the ternary Zn<sub>1-x</sub>Mg<sub>x</sub>O could be utilized as a barrier layer [1]. Moreover, the application of Zn<sub>1-x</sub>Mg<sub>x</sub>O to the window layer of solar cells can improve the overall efficiency by decreasing the absorption loss [2]. A large number of reports have intended to enhance the band gap of ZnO by alloying with different concentrations of MgO [3, 4]. The solid solubility of MgO in ZnO was reported to be 33 mol% for the thin film alloys. Since Zn<sub>1-x</sub>Mg<sub>x</sub>O containing MgO over 4 at% is in a thermodynamically metastable state [5], this result indicates that the solubility limit of Mg in ZnO depends on growth mechanisms as well as growth conditions. Despite the potential for the realization of growth of Zn<sub>1-x</sub>Mg<sub>x</sub>O films, previous methods might have disadvantages in mass production, due to their high cost and low throughput. Compared to those methods, the spin coating-pyrolysis technique is known to have the distinct advantages of low cost, process simplicity, and ease of doping. In this work, polycrystalline Zn<sub>1-x</sub>Mg<sub>x</sub>O films on slide glass substrates have been prepared by CSD.

### Experimental Procedure

Zn<sub>1-x</sub>Mg<sub>x</sub>O (x ranging from 0 to 0.50) films with different Mg contents were prepared by CSD. Zn- and

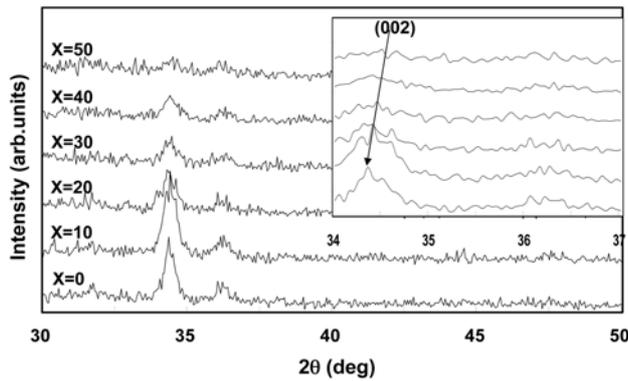
Mg-naphthenates in toluene, were chosen as the sources of zinc and magnesium, respectively. As a substrate, we used a well-polished soda-lime-silica glass (SLSG) plate. The coating sol was dropped and spin-coated at 2000 rpm for 10 s in air. The precursor film was then pre-fired in air at 500 °C for 10 minutes. The coating process was repeated five times. A final annealing was performed at 500 °C for 30 minutes in air.

Characterization of ZnO films by high resolution X-ray diffraction (HRXRD)(X'pert-PRO, Philips, Netherlands) was carried out. Transmittance in the visible wavelength range was observed using a UV spectrophotometer (Cary 500 Scan, Varian, Australia). The thickness of the annealed films was approximately 0.6~0.7 μm, as determined by observation of fracture cross-sections using a field emission-scanning electron microscope (FE-SEM, S-4700, Hitachi, Japan). The surface roughnesses of the films were studied with a scanning probe microscope (SPM, XE-200, PSIA, South Korea).

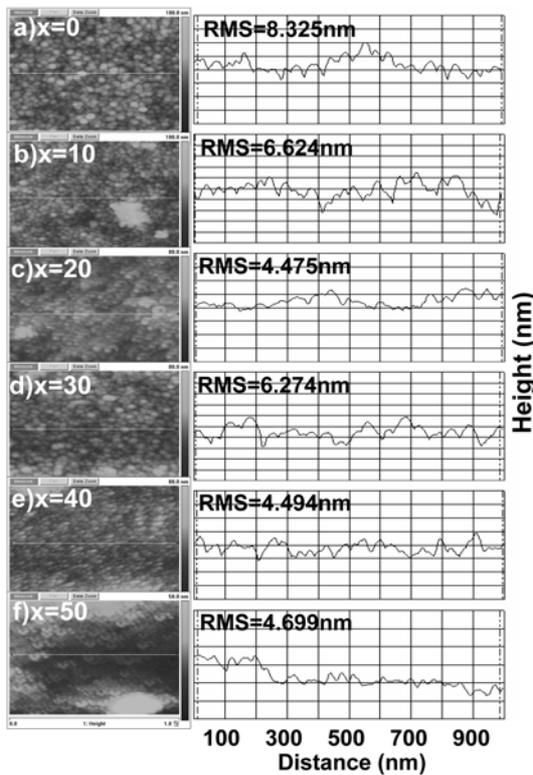
### Results and Discussion

The XRD patterns in Fig. 1 reveal that all the films are composed of wurtzite-type ZnO phase without any impurity phase (e.g., cube-type MgO phase). The maximum Mg content x = 0.5 is larger than the thermodynamic solubility limit (x = 0.04) [5]. Polycrystalline films exhibit three main peaks, which correspond to (100), (002), (101) reflections of the ZnO wurtzite phase. The intensity of (002) peaks becomes weaker as the Mg content increases, which is a similar result in a previous report [4]. As the ionic radii of Mg<sup>2+</sup> (0.57 Å)

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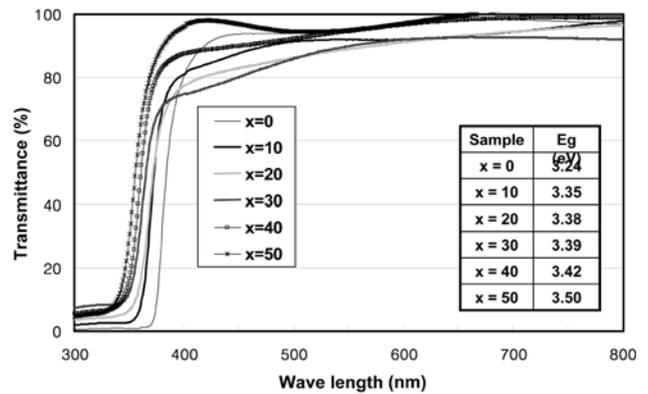
**Fig. 1.** XRD patterns of the  $Zn_{1-x}Mg_xO$  thin films grown on SLSG substrates as a function of Mg content. The insert shows the (002) peak position of the films as a function of Mg content.



**Fig. 2.** Surface roughnesses of the  $Zn_{1-x}Mg_xO$  thin films grown on SLSG substrates as a function of Mg content.

and  $Zn^{2+}$  ( $0.60 \text{ \AA}$ ) have nearly identical values, the strain caused by the replacement of each ion can be relaxed. With an increase in the Mg content, the (002) peak slightly shifted to a higher diffraction angle, as shown in Fig. 1. This shift suggests that the spacing of the plane narrows as the Mg content increases, i.e., the  $a$ -axis length increases with increasing Mg content, while the  $c$ -axis length decreases.

Figure 2 shows the surface roughness of the  $Zn_{1-x}Mg_xO$  thin films as a function of Mg content. The 2D-SPM images of  $Zn_{1-x}Mg_xO$  films show a relatively uniform surface with a surface roughness from 4.494 nm to 8.325 nm.



**Fig. 3.** Optical transmission spectra of the  $Zn_{1-x}Mg_xO$  thin films grown on SLSG substrates as a function of Mg content.

The transmittance of  $Zn_{1-x}Mg_xO$  films was nearly the same as that for ZnO in the visible and near infrared spectral range, as shown in Fig. 3. When the Mg content was increased to  $x = 0.50$ , the slope was still maintained near the absorption edge. This suggests that the crystal structure of  $Zn_{1-x}Mg_xO$  films is probably maintained even in the area of excessive Mg content, although the (002) reflection becomes weaker as the Mg content increases as shown in Fig. 1. For all the films, the average transmittance for the visible wavelength region ( $\lambda = 400\text{--}800 \text{ nm}$ ) was more than 85%, as shown in Fig. 3. The transmittance spectra of the films can be analyzed such that the excitonic nature of the films is clearly apparent in the spectra. Because the excitonic binding energy is almost the same as that of ZnO ( $\approx 60 \text{ meV}$ ) in the  $Zn_{1-x}Mg_xO$  thin films [3], the excitonic peak remains present for all compositions with increasing Mg concentration. There is an obvious shift of the absorption edge to shorter wavelengths with increasing Mg content.

The absorption coefficient  $\alpha$  of the films can be calculated from the transmittance using the relationship [6, 7]:

$$\alpha = -(1/t)\ln T,$$

where  $T$  is the transmittance, and  $t$  is the film thickness. It is well known that the absorption coefficient  $\alpha$  for allowed direct transitions at a given photon energy  $h\nu$  can be expressed as:

$$\alpha = (h\nu - E_g)^{1/2}$$

where  $h$  is Planck's constant, and  $\nu$  is the frequency of the incident photon. The optical energy bands gaps ( $E_g$ ) were estimated from the plots of  $\alpha^2$  as a function of photon energy ( $h\nu$ ) [6, 7]. As shown in Fig. 3, the optical energy band gap increased with increasing Mg content; the band gap of the films for  $x = 0, 0.10, 0.20, 0.30, 0.40,$  and  $0.50$  were 3.24, 3.35, 3.38, 3.39, 3.42, and 3.50 eV, respectively. In other words, the  $E_g$  of  $Zn_{1-x}Mg_xO$  thin films became wider as the Mg content increased and it can be controlled between 3.24 and

3.50 eV. Therefore the present results clearly indicate that  $Mg^{2+}$  can be doped in to the ZnO lattice by a spin coating-pyrolysis technique using metal naphthenates precursor.

### Conclusions

$Zn_{1-x}Mg_xO$  thin films were successfully prepared on SLSG using metal naphthenate precursors. The thin films are composed of wurtzite-type ZnO phase without any impurity phase, while the intensity of (002) peaks became weaker as the Mg content increased. For all the films, the average transmission in the visible wavelength region was over 85%, and the optical energy band gap of  $Zn_{1-x}Mg_xO$  thin films could be controlled between 3.24 and 3.50 eV by adjusting the Mg content.

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