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# Controlled surface morphology and enhanced optical properties of hot water-treated ZnO film by Mg layer insertion

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Zn film and Zn/Mg multilayered films were subjected to hot water treatment in ultrapure water at 368 K, and treated films were analyzed using X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), and ultraviolet-visiblenear infrared (UV-Vis-NIR) spectrophotometry. Mg layer insertion was shown to enhance the oxidation of Zn and modify surface morphology, resulting in enhanced optical properties as an anti-reflection coating.

Key words: Hot water treatment, Zinc oxide, Oxidation, Anti-reflection coating.

### Introduction

Zinc oxide (ZnO) has been extensively investigated because of its semiconductive and piezoelectric properties [1, 2]. For example, ultraviolet light-emitting diodes based on ZnO film have been reported [3]. Bulk acoustic wave resonators were also fabricated using caxis textured ZnO film, as ZnO exhibits large piezoelectric properties along its c-axis ([001] direction) [4]. In addition, ZnO doped with aluminum (Al) has been examined as a transparent conductive oxide [5].

These various applications stimulate research in fabrication methods, which could be classified into chemical vapor deposition [6, 7], physical vapor deposition [4, 5], chemical synthesis [8], and thermal oxidation [9-11]. The latter method offers high productivity for mass production, as the fabrication of metallic Zn film and the thermal oxidation process could be readily feasible compared to other methods. In addition, the visible luminescence property of ZnO films fabricated by thermal oxidation can be easily controlled by temperature [10]. However, this thermal oxidation method requires annealing at high temperature for oxidation. As an alternative oxidation method, hot water treatment for oxidizing Zn film at a low temperature (368 K) has been examined, and fabricated films have been employed as anti-reflection coatings [12-14]. However, the oxidation rate of hot water treatment (1-2 nm/min for Zn) is low, as the process temperature is only 368 K. Therefore, it is necessary to enhance the reaction rate of this treatment for practical use.

In this study, to accelerate oxidation during hot water

treatment, insertion of a magnesium (Mg) layer into Zn film was examined, as Mg reacts with water [15]. Accordingly, the hot water reaction at 368 K was completed within 10 min. In addition, the surface morphology was modified, and resulted in enhanced optical transmittance.

### Experimental

Zn film and Zn/Mg multilayered films were fabricated using a radiofrequency (RF) sputtering apparatus. To minimize oxygen contamination during multilayer deposition, two 4-inch sputtering cathodes, targets of which were Zn (99.999%) and Mg (99.999%), were placed in the same vacuum chamber and deposition of the multilayer was conducted without breaking the vacuum. The base pressure was better than  $4.0 \times 10^{-5}$  Pa. Argon sputtering gas (99.9995%) was introduced and filled at 1.3 Pa. The same RF sputtering power of 50 W was applied to Zn and Mg cathodes. The reflectance power was almost zero. The distance between the target and substrate was 50 mm. The deposition rates of Zn and Mg were 13.3 and 7.5 nm/min, respectively. The layer structures of prepared Zn/Mg films were  $(Zn(33.3 \text{ nm})/Mg(x \text{ nm}))_3/$ Corning Eagle XG glass substrate, where x = 0.0, 3.3, 6.7, and 10.0 (the specimen of x = 0.0 corresponds to pure Zn film, while others are Zn/Mg multilayered films). The size and thickness of Eagle XG glass were  $20 \text{ mm} \times 15 \text{ mm}$  and 0.7 mm, respectively. The deposited films were subjected to hot water treatment in ultrapure water (resistivity:  $18.2 \text{ M}\Omega \text{ cm}$ ) for 2 hours at 368 K. The ultrapure water was stirred using a magnetic stirrer and the films were placed at the center of a 1000-mL beaker.

The as-deposited and hot water-treated films were analyzed using X-ray diffraction (XRD) (RU-300;

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Rigaku Co.) equipped with a rotating copper anode. The diffractometer was operated at 40 kV-200 mA, and the diffracted Cu $K_{\alpha}$  X-rays were counted using a scintillation counter with a graphite monochromator. The diffraction intensity profiles were collected at the  $\theta$ -2 $\theta$ configuration (rate: 0.18 °/min). Surface morphologies of films were observed by field emission scanning electron microscopy (FE-SEM) (S-4200; Hitachi High-Technologies Co.) operated at 5 kV. Optical properties of films were measured using ultraviolet-visible-near infrared (UV-Vis-NIR) spectrophotometry (UV-3100PC; Shimadzu Co.). Using the integrated sphere, total transmittance was recorded as a function of wavelength.

## **Results and Discussion**

Figure 1 shows as-deposited and hot water-treated  $(Zn(33.3 \text{ nm})/Mg(x \text{ nm}))_3$ /substrate. The as-deposited films exhibited metallic luster (Fig. 1(a)-(d)), while the hot water-treated films were transparent (Fig. 1(e)-(h)). According to the observations during hot water treatment, although the total amount of Zn in prepared Zn/Mg films was identical to 100 nm in thickness, the reaction from metal to oxide was finished within 90, 60, 20, and 10 min for x = 0.0, 3.3, 6.7, and 10.0, respectively. Thus, Mg layer insertion enhances the reaction between Zn and water.

For further investigation of the effects of Mg layer insertion, XRD profiles were measured (Fig. 2(a)). The results confirmed that both as-deposited Zn and Zn/Mg films consist of metallic hexagonal close-packed (hcp) Zn crystals (a = 0.2665 nm, c = 0.4947 nm) [16]. However, the peak intensity of  $(002)_{Zn}$  was changed by Mg layer insertion: Zn film without Mg layer exhibited a stronger  $(002)_{Zn}$  peak compared to Zn/Mg films. Therefore, insertion of the Mg layer suppresses (001) the texture of Zn and the other planes with higher *hkl* indices, which have higher reactivity than the (001) plane, are exposed to the surface. Accordingly, the



**Fig. 1.** Pictures of as-deposited and hot water-treated  $(Zn(33.3 \text{ nm})/Mg(x \text{ nm}))_3/Eagle XG glass substrate. (a), (b), (c), and (d) are as-deposited films of <math>x = 0.0, 3.3, 6.7, \text{ and } 10.0,$  respectively. (e), (f), (g), and (h) are corresponding hot water-treated films.



Fig. 2. XRD profiles of (a) as-deposited and (b) hot water-treated  $(Zn(33.3 \text{ nm})/Mg(x \text{ nm}))_3/Eagle XG glass substrate.$ 



**Fig. 3.** FE-SEM images of as-deposited and hot water-treated  $(Zn(33.3 \text{ nm})/Mg(x \text{ nm}))_3/Eagle XG glass substrate. (a), (b), (c), and (d) are as-deposited films of <math>x = 0.0, 3.3, 6.7, \text{ and } 10.0,$  respectively. (e), (f), (g), and (h) are corresponding hot water-treated films.

enhanced hot water reactivity could be observed in Zn films with Mg layer insertion. In addition, as Mg dissolves readily in water, the openings originated from Mg layer dissolution also offer additional reaction sites. It should be noted that no peak from Mg was detected, which could be attributed to the relatively small X-ray scattering factor of Mg and/or its low crystallinity.

XRD profiles of hot water-treated films are shown in Fig. 2(b) and all peaks are indexed using hexagonal



Fig. 4. Wavelength dependence of total transmittance of asdeposited and hot water-treated  $(Zn(33.3 \text{ nm})/Mg(x \text{ nm}))_3/Eagle XG glass substrate.$ 

ZnO (a = 0.3250 nm, c = 0.5207 nm) [17]. As the observed peak shifts are less than the error range of the diffractometer (0.05 °), the amount of incorporated Mg into ZnO may be insignificant.

The effects of Mg layer insertion on surface morphologies were investigated using FE-SEM. According to the images (Fig. 3), as-deposited films exhibited island growth and the grain sizes varied from 20 nm to 150 nm. In contrast, Mg layer insertion resulted in relatively uniform nucleation and grain growth (grain size: 60-100 nm). After hot water treatment, the surface was modified and Mg layer insertion resulted in nonaggregated growth of rod-like ZnO crystals, while aggregated rose flower-like ZnO was formed from Zn film without the Mg layer. This may be related to the texture of as-deposited films: as high Miller index planes are deposited in the case of Zn films with Mg layer insertion, ZnO crystals grow along various directions, as shown in Fig. 3(h). In addition, it seems that surface roughness increases with Mg content.

Optical properties correspond with the surface morphology (Fig. 4). In the case of as-deposited films, total transmittance was decreased in accordance with Mg layer insertion, which may be related to uniform island growth by Mg layer insertion. After hot water treatment, total transmittance of films exceeded the glass substrate, which could be explained by the gradient refractive index structure [18-20]. The highest total transmittance in the wavelength region of 0.6-1.5  $\mu$ m was achieved in the case of Zn film with insertion of a Mg layer 10 nm thick, which corresponds to the surface morphology observed by FE-SEM (Fig. 3(h)). Thus, Mg layer insertion enhances the optical

properties and hot water-treated Zn/Mg films can be applied as anti-reflection coatings.

#### Conclusions

Zn and Zn/Mg films were subjected to hot water treatment in ultrapure water, and the treated films consisted of ZnO. The Mg layer insertion resulted in suppression of (001) preferred orientation, uniform island growth, and provision of additional reaction sites. Accordingly, hot water treatment was completed within 10 min, and the film surface morphology was also modified, resulting in enhanced anti-reflection coating properties. Thus, the multilayered film with Mg layer insertion provides high hot water reactivity and better optical properties compared to monolayer films.

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