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Research Article

The Effect of Mg Dopant and Oxygen Partial Pressure on Microstructure and Phase Transformation of $ZnTiO_3$ Thin Films

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Mg-doped zinc titanate ($ZnTiO_3$) films were prepared using RF magnetron sputtering. Subsequent annealing of the as-deposited films was performed at a temperature ranging from 600 to 900°C for 2 hours with a heating rate of 5°C/min in air. It was found that the as-deposited films were amorphous and contained 2.77 at.% magnesium. This was further confirmed by the onset of crystallization that took place at annealing temperatures of 600°C. The results showed that single $Zn_2Ti_3O_8$ phase was existed at 600°C. When annealing is at 700°C, the results revealed that mainly a hexagonal $ZnTiO_3$ phase accompanying a $Zn_2Ti_3O_8$ minor phase was observed. When annealing is at 900°C, the results showed that single hexagonal $ZnTiO_3$ phase is stable at 900°C. It means that $ZnTiO_3$ phase containing no Mg is unstable at 900°C and is decomposed from hexagonal $ZnTiO_3$ to cubic Zn_2TiO_4 and rutile TiO_2 at 900°C. In addition, the effect of oxygen partial pressure for the films deposited on the phase transformations and microstructures of zinc titanites thin film was investigated.

1. Introduction

As the need for versatile electronic components with high reliability increases, the development of high-frequency electronic materials becomes imperative. Zinc titanate ($ZnTiO_3$) has been reported to have specific electrical properties that are adequate for applications in microwave dielectrics [1–3]. The ZnO-TiO_2 system exists in three forms: zinc metatitanate ($ZnTiO_3$) with a hexagonal ilmenite structure; zinc orthotitanate (Zn_2TiO_4) with a cubic spinel crystal structure; zinc polytitanate ($Zn_2Ti_3O_8$) with a cubic defect spinel structure [4]. Steinike and Wallis. [5] have reported on $Zn_2Ti_3O_8$ materials, a low-temperature form of $ZnTiO_3$ existing at temperature <820°C. The $Zn_2Ti_3O_8$ compound was formed based on the Zn_2TiO_4 phase [6]. However, hexagonal $ZnTiO_3$ decomposes into cubic Zn_2TiO_4 and rutile TiO_2 at T >945°C [7]. Moreover, a $ZnTiO_3$ single-phase compound can be prepared by zinc oxide and rutile hydrate at T = 850 ~ 900°C [4].

Pure $ZnTiO_3$ shows good dielectric properties in the microwave range. It has a perovskite-type oxide structure and could be advantageous as a microwave resonator material [8]. Furthermore, $ZnTiO_3$ can be sintered at 1100°C without the use of sintering aids [7, 8]. Moreover, when a sintering aid is added, it can be fired at temperatures below 900°C [9, 10]. $ZnTiO_3$ has potential applications in gas sensors that detect ethanol or carbon monoxide. It is also a promising candidate for the use in nonlinear optics, as a luminescent material and in various photocatalytic roles [11, 12].

Pure zinc titanate thin films have been prepared by RF magnetron sputtering in previous studies [13]. It was shown that crystallization of the $ZnTiO_3$ phase occurred at a substrate temperature of 400°C and annealing temperature of 700°C over 2 h. However, as the annealing temperature exceeded 900°C, the ilmenite $ZnTiO_3$ decomposed into cubic Zn_2TiO_4 and rutile TiO_2. In the present work, to suppress $ZnTiO_3$ decomposition at 900°C, Mg-doped zinc titanate thin films were prepared by RF magnetron sputtering. The microstructure and phase transformation of Mg-doped zinc titanate thin films with different annealing temperatures were subsequently investigated. In addition, the impact of different atmosphere (Ar/O_2 ratio) during sputtering was investigated.

Table 1: RF sputter conditions for the magnesium zinc titanate films.

Target	$(Zn_{0.95}Mg_{0.05})TiO_3$
Substrates	SiO_2/Si
Target size in diameter (mm)	76.2
Target to substrate distance (mm)	90
RF power (W)	150
Chamber pressure (Pa)	6.6×10^{-4}
Working pressure (Pa)	2.5
Sputtering gas	Ar
Ar flow (sccm)	50
Substrate temperature (°C)	400
Deposition time (min)	120
Deposition rate (nm/min)	1.4
Substrate bias	Grounded

2. Experimental Procedure

The Mg-doped zinc titanates thin films were prepared by RF magnetron sputtering with the deposition conditions listed below.

A bulk magnesium zinc titanate target was synthesized by conventional solid-state methods from high-purity oxide powders; MgO, ZnO, and TiO_2 (>99.9%). The starting materials were mixed according to the stoichiometry of $(Zn_{0.95}Mg_{0.05})TiO_3$. The powder was then sintered and pressed into disks with a diameter of 76.2 mm and thickness of 3 mm. These were subsequently used as $(Zn_{0.95}Mg_{0.05})TiO_3$ targets. The Mg content in the zinc titanate thin films was analyzed using electron spectroscopy for chemical analysis (ESCA), showing that the as-deposited thin films contained 2.77 at.% Mg.

Magnesium zinc titanate thin films were fabricated onto SiO_2/Si substrates using a 13.56 MHz, 150 W RF magnetron sputtering system. The sputtering chamber was evacuated by an oil diffusion pump to a base pressure of 6.6×10^{-4} Pa. The sputtering gas Ar flow of 50 sccm with a purity of 99.999% was introduced into the chamber with mass flow controllers and a working pressure of 2.5 Pa. The target was cleaned at an RF power of 100 W for 5 min in an atmosphere of pure Ar, and the substrate was covered with the shelter. The films were deposited at 400°C of substrate temperature. The as-deposited films were annealed at 600 to 900°C for 2 hours with a heating rate of 5°C/min in air. The detailed deposition conditions of the zinc titanate films are listed in Table 1. For the different atmosphere, (Ar/O_2 ratio) during sputtering was also carried out, the gas ($Ar + O_2$) flow was fixed at 50 sccm. The O_2 gas flow was changed from 0 to 10 sccm.

Crystallinity of the films was analyzed by X-ray diffraction (XRD, Bruker D8A Germany), with Cu Kα radiation for 2θ from 20° to 80° at a scan speed of 3° min^{-1} and a grazing angle of 0.5° under 40 kV and 40 mA. The DIFFRAC plus TOPAS version 3.0 program was used to determine the lattice parameters. Microstructural and thickness observations of the cross-section and plane-view morphology of the thin films grown on SiO_2/Si (100) substrates were analyzed using field-emission scanning electron microscope (FE-SEM, Hitachi S-4700 Japan). Microstructure of the films and the $ZnTiO_3/SiO_2$ interfaces were investigated by filed-emission transmission electron microscopy (FE-TEM, FEI E.O. Tecnai F20) at an acceleration voltage of 200 kV, equipped with energy-dispersive spectroscopy (EDS). Atomic force microscopy (AFM, Veeco CP-II) was used to study the surface topography, with a scanned area of 5 μm × 5 μm.

3. Results and Discussion

3.1. The Effect of Mg Dopant on the Phase Transformation of $ZnTiO_3$ Thin Film. Figure 1 (a) shows the X-ray diffraction (XRD) patterns of the 2.77 at.% Mg-doped zinc titanate thin films annealed at 600, 700, 800, and 900°C. It was observed that the as-deposited thin films were amorphous, indicating that no crystallization occurred in the as-deposited thin films. At 600°C, the $Zn_2Ti_3O_8$ peaks appeared, which is a low-temperature form of ZnO-TiO_2 system, as reported by Yamaguchi et al. [14]. $Zn_2Ti_3O_8$ is a stable or metastable compound; its existence was first reported by Bartram and Slepetys [4], who found that it decomposes at temperatures above 700°C, and $Zn_2Ti_3O_8$ can be existed stably between 600 to 700°C [4, 6]. However, the intensity of peaks increased rapidly up to 700°C. The majority crystalline phase was identified as hexagonal $ZnTiO_3$, accompanied by $Zn_2Ti_3O_8$ minor phases.

As the annealing temperature was increased to 800°C, the hexagonal $ZnTiO_3$ became a single crystalline phase. The intensity of the (104) peak was higher than the other peaks of the $ZnTiO_3$ films, indicating that there is a high degree of (104)-oriented $ZnTiO_3$ on the SiO_2/Si(100) substrates. Chen and Huang. [15] have shown that (100)-oriented $MgTiO_3$ films were obtained on the Si substrate. The preferred orientation tends to reduce the free energy to reach a stable state. When the temperature was further increased to 900°C, the $ZnTiO_3$ single phase was remained. This result is unlike pure zinc titanate thin films where the hexagonal $ZnTiO_3$ phase decomposes into TiO_2 and Zn_2TiO_4 at 900°C, as shown in Figure 1 (b).

Figure 2 shows the SEM micrographs of the Mg-doped zinc titanate thin films deposited on SiO_2/Si substrate annealed at different temperatures. The grain size increased with the annealing temperatures. The grain sizes of specimens for 700°, 800°, and 900°C are 25 nm, 139 nm, and 208 nm, respectively. To prove that pure $ZnTiO_3$ phase exist in Mg-doped zinc titanate thin films at 900°C, high resolution TEM was used to analyze these Mg-doped $ZnTiO_3$ thin films. Figure 3 shows the cross-section of Mg-doped $ZnTiO_3$ thin films on a SiO_2/Si substrate. The HRTEM of region 1 and 2 shows the d-spacing of h-$ZnTiO_3$ phase, which is d_{003}= 0.441 nm and 0.449 nm, respectively. The XRD analysis revealed a similar trend. Comprehensively, the results confirmed that $ZnTiO_3$ thin films were successfully prepared at 900°C. Interestingly, a twin is observed as shown in Figure 3 (a), this is a two-dimensional defect. A twin is defined as a region in which a mirror image of the structure exists across a plane or a boundary. This defect is often due to an atomic lattice defect forming a mirror image of

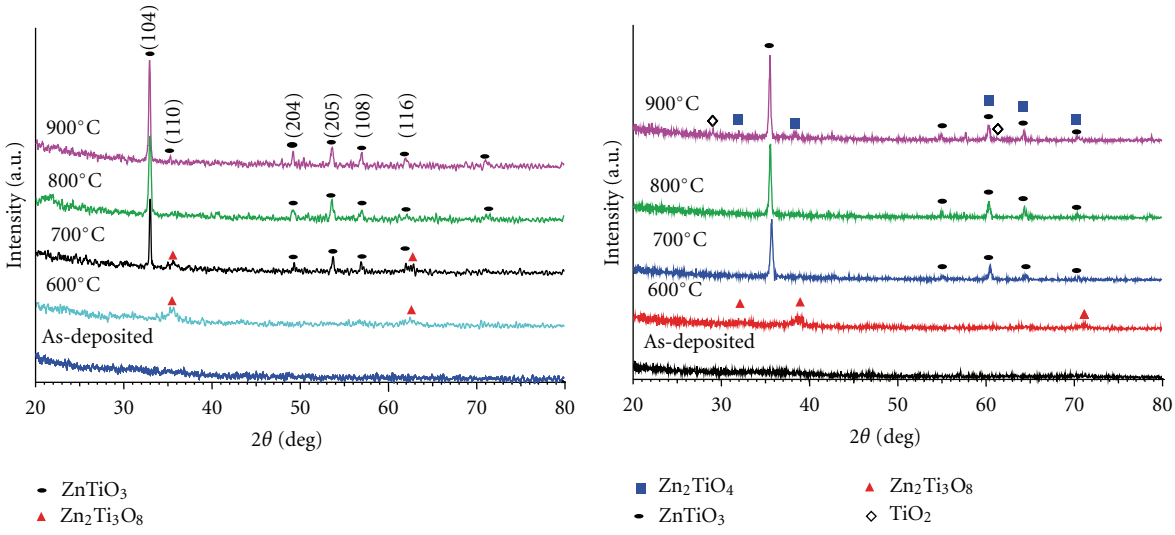

Figure 1: X-ray diffraction patterns of thin films annealed at different temperatures, (a) Mg-doped zinc titanates thin film and (b) pure zinc titanates thin film.

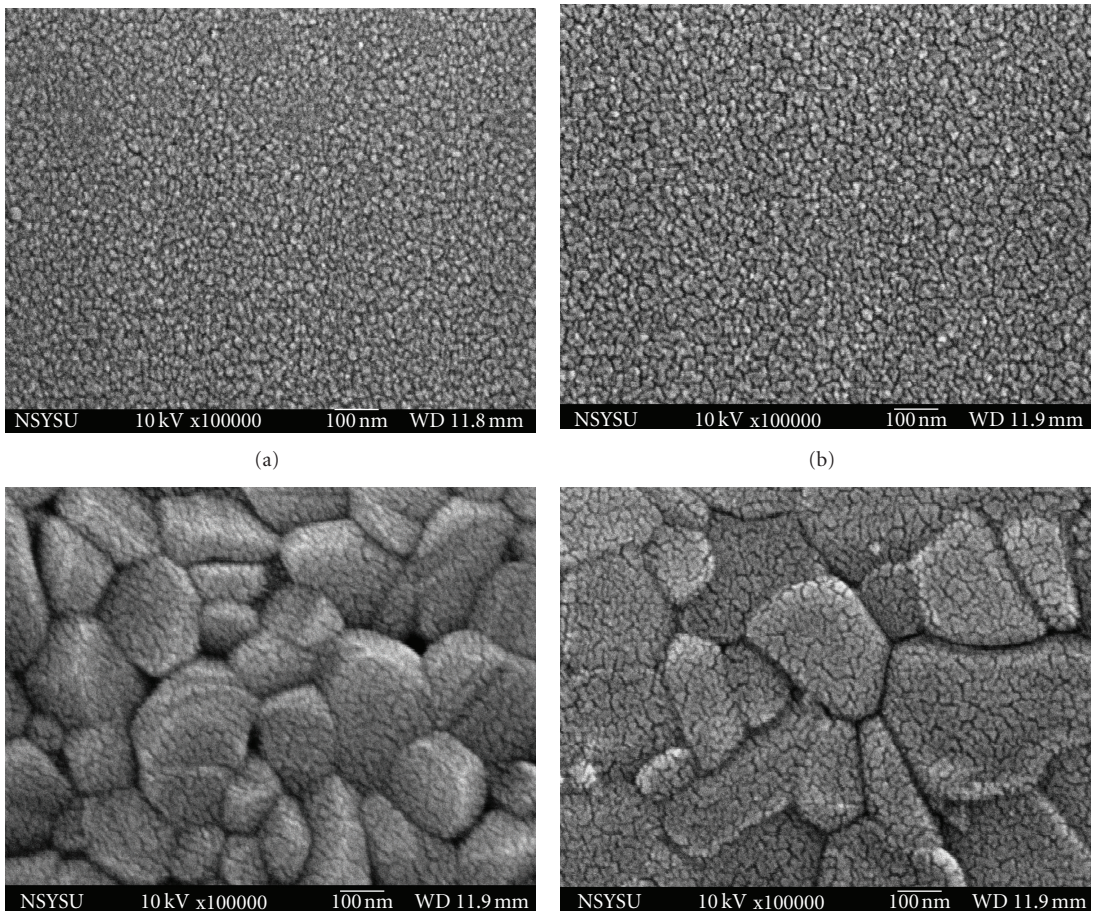

Figure 2: The SEM micrographs of Mg-doped zinc titanates thin films annealed at (a) as-deposited, (b) 700°C, (c) 800°C, and (d) 900°C.

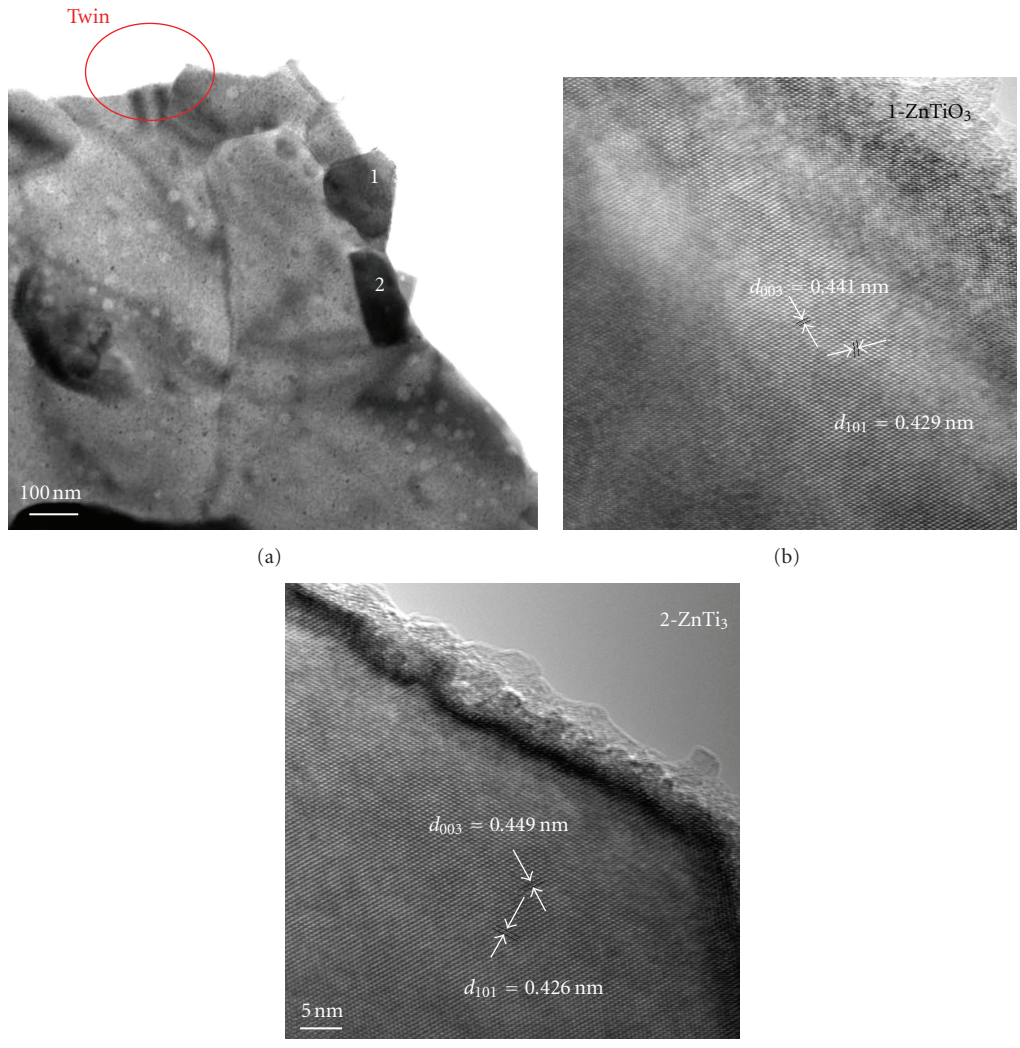

FIGURE 3: TEM micrographs of the zinc titanates thin films with Mg dopant annealed at 800°C. (a) Twin, (b) region 1 of $ZnTiO_3$ grain, and (c) region 2 of $ZnTiO_3$ grain.

undeformed lattice next to it. Based on the above results, it can be expected that the Zn atoms are substituted with Mg atoms in the ABO_3 structure. This may be attributed to the ionic radius of Mg^{2+} (0.66 Å), which is smaller than that of Zn^{2+} (0.74 Å) [16, 17]. Hence, when Mg^{2+} substitutes on Zn^{2+} sites in the ABO_3 structure, lattice strain will be created.

3.2. The Effect of Oxygen Partial Pressure on the Phase Transformation of $ZnTiO_3$ Thin Film. The effect of oxygen partial pressure on the phase transformation of zinc titanates thin films was also investigated. The different atmosphere (Ar/O_2 ratio) during sputtering was carried out in this experiment. Table 2 lists the element analysis of zinc titanites thin films using ESCA equipment. It is found that the Zn/Ti ratio decreased significantly when O_2 was used in the chamber. The compositions at different oxygen partial pressures are different from target composition, which results from the different striking coefficients and variation in sputtering yields of the constituent elements [18]. During sputtering, the target atoms are subject to collisions with gas atoms or molecules left in the chamber and other ejected atoms, resulting in a partial loss of energy and direction on their way to the substrate [19]. Because oxygen gas is biatom molecule and its radius is much larger than Ar, the sputtered particles suffer from more collision when more oxygen partial pressure is introduced. This changes the composition of thin film.

XRD measurements were performed to examine the variation of structural properties with varying oxygen partial pressures (P_{O2}). Figure 4 shows the XRD spectra of zinc titanate thin films grown under different Ar and O_2 ratios, and these films were annealed at 800°C. For an Ar/O_2 ratio of 9 : 1 (10% O_2), the $ZnTiO_3$ and $Zn_2Ti_3O_8$ phases coexisted as shown in Figure 4 (b). This result indicates that 10% O_2 in the sputtering atmosphere leads to the remaining $Zn_2Ti_3O_8$ phase at 800°C, because the $Zn_2Ti_3O_8$ phase is stable

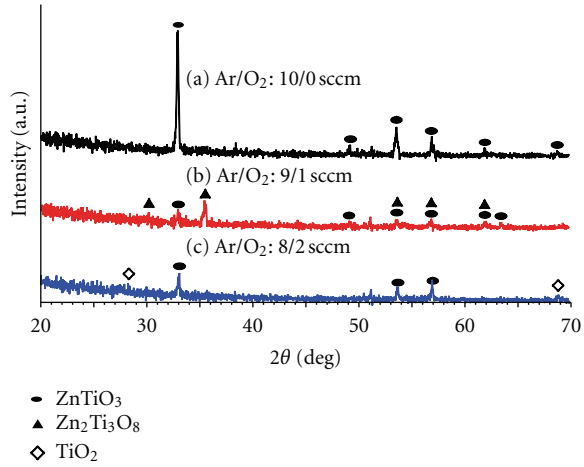

Figure 4: X-ray diffraction patterns of the zinc titanates thin films deposited at RF power: 200 W, substrate temperature of 400°C, and then annealed at 800°C with different Ar to O_2 ratio (a) 10 : 0, (b) 9 : 1 and (c) 8 : 2.

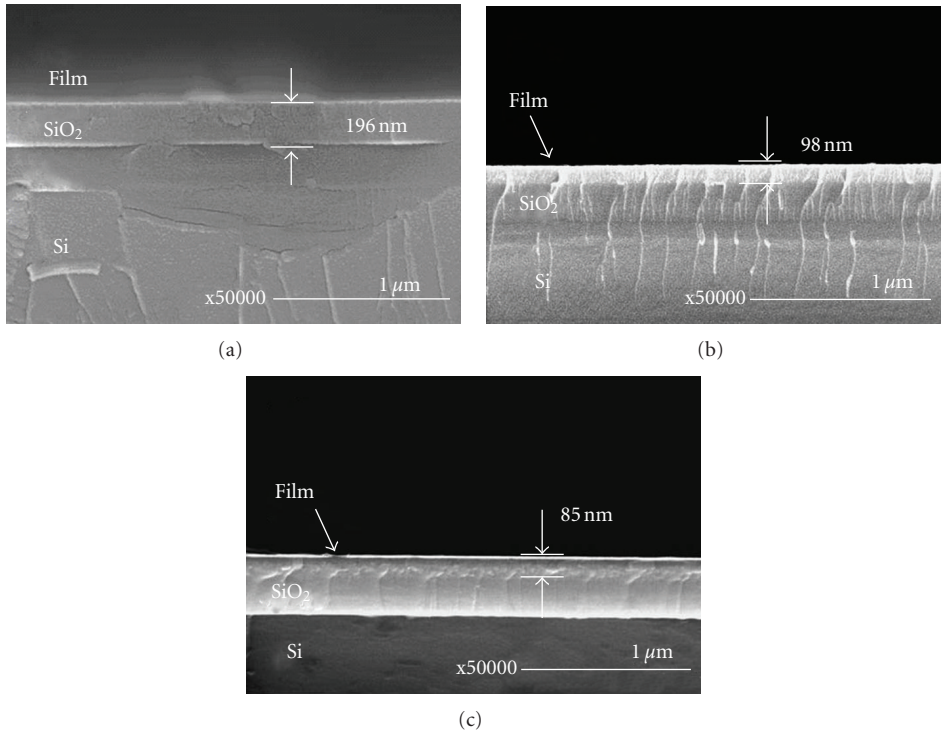

Figure 5: The film thickness of the zinc titanate deposited at 400°C of substrate temperature and then annealed at 800°C with different Ar to O_2 ratio (a) 10 : 0, (b) 9 : 1, and (c) 8 : 2.

Table 2: The elements analysis of zinc titanate thin films at different oxygen partial pressure was measured using ESCA equipment.

Substrate temperature (°C)	Oxygen partial pressure (Ar to O_2 ratio)	Surface element composition, X%			Zn/Ti
		Zn2p	Ti2p	O1s	
400	50/0 (10 : 0)	13.23	20.55	63.19	0.64
400	45/5 (9 : 1)	11.07	22.22	65.57	0.50
400	40/10 (8 : 2)	12.23	20.92	65.41	0.58

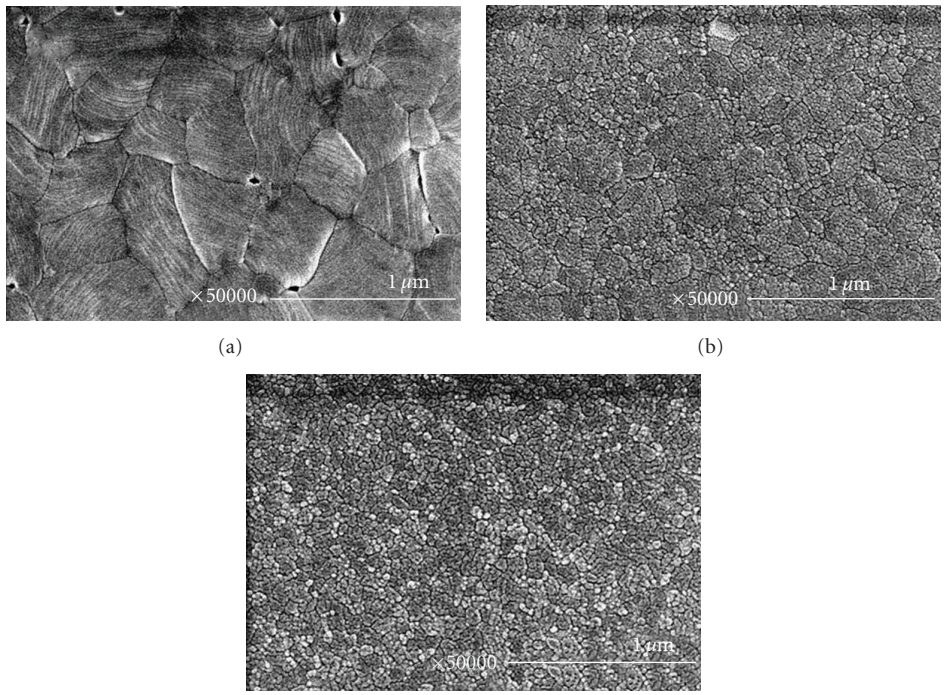

Figure 6: Plane-view SEM micrographs of zinc titanate thin film deposited at 400°C of substrate temperature and then annealed at 800°C with different Ar to O_2 ratio (a) 10 : 0, (b) 9 : 1, and (c) 8 : 2.

below 700°C without oxygen in the atmosphere, as seen in Figure 4 (a). However, when the O_2 partial pressure was increased to 20% (Ar/O_2 ratio of 8 : 2), the major and minor phases were $ZnTiO_3$ and TiO_2 phases, respectively. This result indicates that 20% O_2 in the sputtering atmosphere leads to the decomposition of the $Zn_2Ti_3O_8$ phase into $ZnTiO_3$ and TiO_2 at 800°C as shown in Figure 4 (c). Hence, there are two phases present at 800°C when O_2 is used: $Zn_2Ti_3O_8$ and TiO_2. According to the phase diagram of ZnO-TiO_2 [4], TiO_2 appears at 945°C and $Zn_2Ti_3O_8$ exists below 700°C. It is believed that the evolution of the phases is related to the variation of oxygen partial pressure. From Table 2, it is noticed that the oxygen partial pressure causes the compositional change of zinc titanates thin films. The variation in composition (especially Zn concentration) may result in the different phase transformations: lower Zn concentration leads to form $Zn_2Ti_3O_8$ or TiO_2. In addition, Zn concentration in zinc titanates thin film may be reduced again during annealing, because zinc is easy to vaporize at high temperature. Therefore, it cannot be formed a $ZnTiO_3$ due to lower Zn concentration.

The film thickness with varying O_2 partial pressure (P_{O2}) was measured using the cross-section of FE-SEM micrographs as shown in Figure 5. The cross-sectional views show that the thicknesses of the films significantly decrease when a small amount of oxygen is added to the sputtering ambient and subsequently decreases slowly as the oxygen partial pressure increases. The thicknesses of the films were 196, 98, and 85 nm for pure Ar and Ar: O_2 flow ratios of 9 : 1 and 8 : 2, respectively. The gradual decrease in thickness with increase of the oxygen partial pressure can be explained by the smaller sputtering yields of oxygen ions than argon ions; the momentum transfer of oxygen is smaller than that of argon during ionic bombardment [20]. However, the thickness difference between the films that are grown with and without oxygen is too significant to be explained only by the momentum transfer process [21]. In addition, according to XRD analysis (Figure 4), increasing the oxygen partial pressure was found to degrade the crystallinity of the zinc titanites thin films due the formation of oxygen-induced defects [22, 23].

Plane-view SEM micrographs of zinc titanate thin film deposited at 400°C substrate temperature and then annealed at 800°C with different Ar to O_2 ratio are shown in Figure 6. As one can see, the grain size decreased with increasing O_2 partial pressure. According to XRD analysis, the phases of the thin film also differ with O_2 partial pressure. Moreover, it is found that there are two kinds of grains in the 10%P_{O_2} samples as shown in Figure 6 (b). According to XRD analysis (Figure 4), $ZnTiO_3$ grains and $Zn_2Ti_3O_8$ grains are identified. The surface morphologies of zinc titanite films have been observed with AFM, and the results are shown in Figure 7, corresponding to the samples prepared at oxygen partial pressures of 0% and 10%. The left figures display the surface morphologies and the pictures on the right depicts typical three-dimensional representations (1000 nm by 1000 nm surface plots). All the films present a rough surface texture, consisted of particles fused together, building up high mountains and deep valleys. All the films can be described as a contiguous network of particles and aggregates

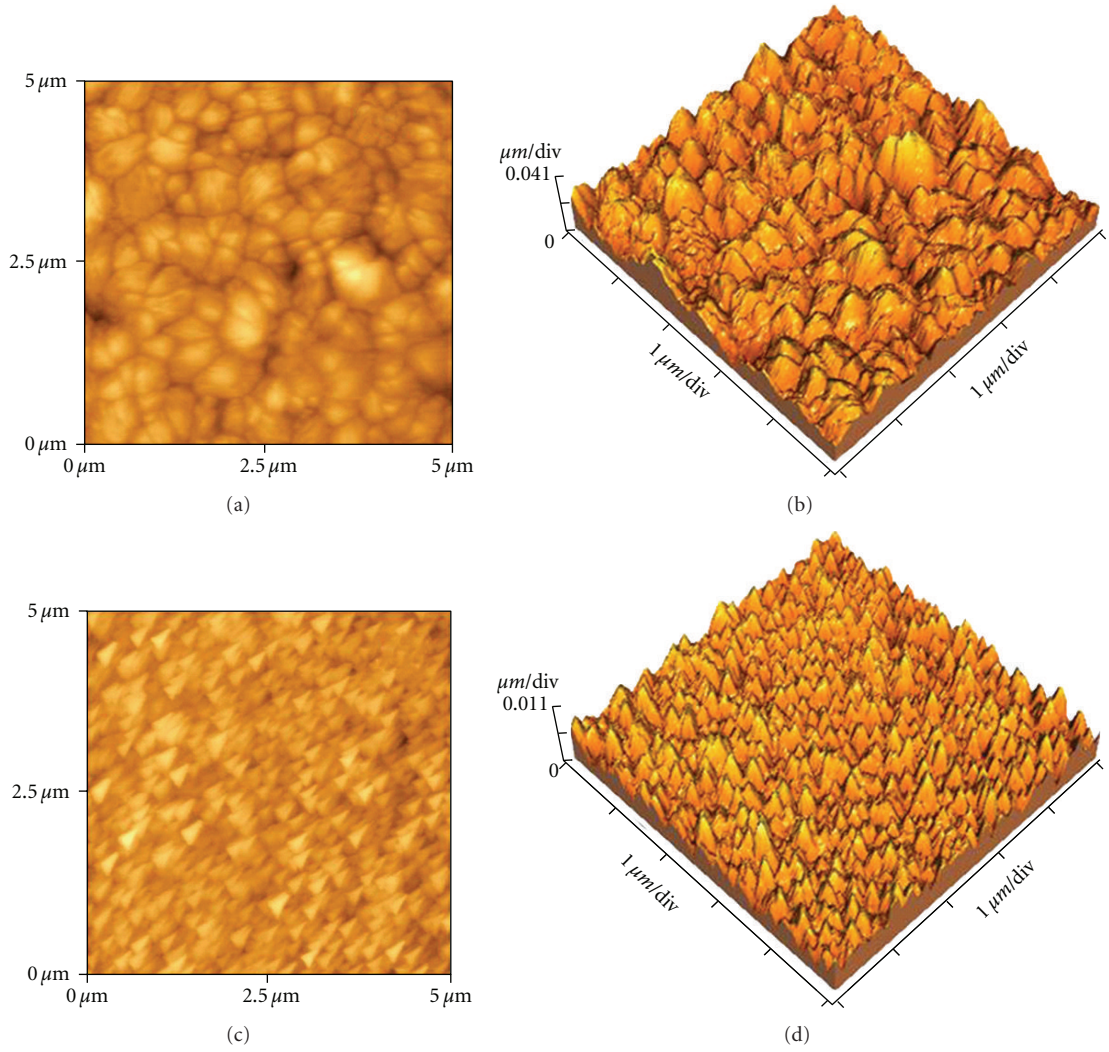

Figure 7: AFM surface morphologies and the right pictures depict typical three-dimensional representations (1000 nm × 1000 nm surface plots) of the zinc titanate thin films deposited at 400°C of substrate temperature and then annealed at 800°C: (a) and (b) Ar to O_2 ratio 10 : 0, and (c) and (d) Ar to O_2 9 : 1.

with significant roughness. It is also shown that the TiO_2 particles decrease in size with an increase in oxygen partial pressure, which may be ascribed to the deposition rate.

4. Conclusion

The effects of Mg doping on zinc titanate thin films were investigated using a variety of analytical tools. The microstructure and phase transformation of zinc titanate thin films can be influenced by doping Mg. It is found that the as-deposited films were amorphous, as confirmed by the XRD results. The results showed that single $Zn_2Ti_3O_8$ existed when the films were annealed at 600°C. When annealing was conducted at 700°C, the results revealed that the majority phase was hexagonal $ZnTiO_3$, accompanied by minority amounts of $Zn_2Ti_3O_8$. Unlike pure zinc titanate films, this result shows that the $Zn_2Ti_3O_8$ phase can exist at temperatures above 700°C. However, there is no decomposition from hexagonal $ZnTiO_3$ to cubic Zn_2TiO_4 and rutile TiO_2 took place with a further increase in temperature to 900°C. It means that the addition of Mg to $ZnTiO_3$ compound increases its stability up to 900°C. In addition, with increasing oxygen partial pressure (Ar-to-O_2 ratio decreased from 10 : 0 to 8 : 2), the phase transformations versus temperatures changed. At an Ar-to-O_2 ratio of 9 : 1, $ZnTiO_3$ and $Zn_2Ti_3O_8$ phases coexisted at 800°C. By increasing the P_{O2} partial pressure to 8 : 2, the $ZnTiO_3$ phase remained as the main phase, accompanied by a TiO_2 minor phase at 800°C

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