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Dielectric properties of zinc titanate thin films prepared by Rf magnetron sputtering

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Abstract Zinc titanate thin films of ~500 nm in thickness were synthesized by an RF magnetron sputtering using a sintered ceramic target. After annealing in temperature ranges of 300–800 °C, their phase transition and dielectric properties were investigated as a function of annealing temperature. Crystalline $ZnTiO_3$ phase was first detected at the annealing temperature of 500 °C within XRD detection limit though the sputtered film was mainly amorphous. $ZnTiO_3$ still remained as a main phase although the slight decomposition of $ZnTiO_3$ into Zn_2TiO_4 and TiO_2 occurred in association with the increase of annealing temperature. Dielectric properties were apparently improved with increase of annealing temperature and showed maximum value at 650 °C. Further higher temperature annealing caused inferior dielectric property. These results were explained in terms of the presence of TiO_2 (rutile) phase, resulting from the decomposition of $ZnTiO_3$ phase, and the morphology of the thin film.

Keywords Zinc titanate · Thin film · RF sputtering · XRD · Dielectric property

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1 Introduction

Basic studies regarding the phase diagram and the physical properties of ZnO–TiO2 system have been published since 1960s [1, 2]. Much attention has been still paid because of its diverse electrical and chemical properties, leading to the wide applications in sensors, microelectronics and high performance catalysts [3–6]. Recently, the zinc titanate ceramics have been promisingly reported as microwave dielectric materials due to their stable and proper dielectric properties [7–9]. Dulin and Rase [1] showed that three compounds exist in the $ZnO–TiO_2$ system, including Zn_2TiO_4 (cubic), $ZnTiO_3$ (hexagonal), and $Zn_2Ti_3O_8$ (cubic). Zn_2TiO_4 phase can easily be prepared by conventional solid-state reaction. While, the stable formation of $ZnTiO_3$ phase was known to be complicated, mainly due to the decomposition of $ZnTiO_3$ into Zn_2TiO_4 and rutile at about 945 °C [1]. Several reports are evident in the literature on the characteristics of $ZnTiO_3$ powder prepared by solid state reaction and sol–gel methods [6, 10, 11]. Kim et al. and other researchers [7, 8, 12, 13] also tried to obtain the suitable dielectric properties by controlling composition in $ZnO–TiO_2$ binary system and/or substituting zinc with barium, calcium, strontium and magnesium. Most of those studies involve only bulk system. References concerning the characteristics of zinc titanate based thin film are generally lacking, except the report of Chen et al. regarding the zinc titanate thin film prepared by a metalorganic chemical vapor deposition [4, 14]. However their studies only limited to the analyses of phase, composition and microstructure of thin film, especially focusing on Zn_2TiO_4 phase for the catalytic application. In this paper, the authors have attempted to synthesize zinc titanate thin film by RF magnetron sputtering using a solid-state reacted ceramic target. After annealing the films at various temperatures,

their crystal structures were analyzed and dielectric properties were investigated in terms of phase present and microstructure.

2 Experimental procedure

The ZnO–TiO_2 ceramic target for thin film was prepared by a solid-state reaction method using ZnO (99.9%) and TiO_2 (99+%) raw powders. These powders were appropriately weighed to meet the mol ratio of ZnO/TiO_2=1:1, and then milled with yttria stabilized zirconia balls in ethanol for 24 h. Mixtures were dried and calcined at 1000 °C for 2 h. After re-milling and drying the calcined powders, those were mixed with polyvinyl alcohol (PVA) solution as a binder and pressed into discs of 100 φ in diameter and 5 mm thick using cold isostatic press. The pellet was sintered at 1200 °C for 4 h in air. After lapping and polishing, the zinc titanate target was prepared by back-side plate bonding. The crystal structure of the calcined and sintered ceramic pellet was analyzed by X-ray diffractometer (XRD). Zinc titanate thin films with ~500 nm in thickness were deposited onto well-cleaned Pt(150 nm)/Ti(10 nm)/SiO_2(300 nm)/Si substrate by using RF magnetron sputter with a sputtering rate of 1.02 Å/s. The deposited films were heat treated at 300, 500, 600, 650 and 800 °C for 2–4 h in air with a heating rate of 5 °C/min, respectively. The as-grown and annealed thin films were characterized with XRD, AES (auger electron spectroscopy) and AFM (atomic force microscopy). For measuring the electrical property, platinum dot was applied as a top electrode. Impedance analyzer (4294A, HP) and megaohm-meter (SM-8210. TOA) were used to measure their electrical properties, such as capacitance, dielectric loss and resistivity.

3 Results and discussion

$ZnTiO_3$ phase was not detected in the sintered target although stoichiometric composition with ZnO/TiO_2=1:1 was initially reacted. As shown in Fig. 1(a), the prepared ceramic target was consisted of Zn_2TiO_4 and TiO_2, which was attributed to the decomposition of ZnO–TiO_2 ceramics during sintering as reported elsewhere [1, 10]. By using this target, thin film of ~500 nm in thickness was deposited and annealed at 300–800 °C, respectively. Figure 1(b–f) illustrates the XRD profiles for the annealed thin films. The sputtered films annealed up to 500 °C for 4 h are nearly amorphous while some weak crystalline peak identified to be $ZnTiO_3$ phases begins to appear within XRD detection limit. The crystallization temperature was much lower than that of the solid-state reacted system [1], while comparable to that of sol–gel derived process [6, 10]. Figure 1 also shows that increase of the annealing temperature slightly changes the intensity and theta value (2θ) of the crystalline peak. Comparing the standard JCPDS files of $ZnTiO_3$ (85-0547), Zn_2TiO_4 (73-0578) and TiO_2 (73-0317), as the annealing temperature increased above 600 °C, the relative intensity of the peak at 32.5° corresponding to $ZnTiO_3$ decreased. On the other hand, the relative intensity of the peak appeared at 35° containing the mixed phases of $ZnTiO_3$ and Zn_2TiO_4 increased and simultaneously slight increase in the intensity of TiO_2 rutile peak at 27.5° was observed. The mixed peaks near ~35° could be analyzed by an angle enlargement ranging from 34.5° to 36° as shown in Fig. 2, where the peak slightly shifted to lower angle according to the increase of annealing temperature. It may be thought that such peak shift is related to the phase transition from $ZnTiO_3$ to Zn_2TiO_4 with increasing the annealing temperature. It was reported that in the ceramic powder reaction, the $ZnTiO_3$ phase decomposed to from Zn_2TiO_4 and rutile TiO_2 above 945 °C [1, 2]. In the case of sol–gel derived system, such decomposition occurred at relatively lower temperature, 600–900 °C, depending on their processing conditions [8, 11]. The XRD results of this study indicate that the main phase for the sputtered zinc titanate thin film annealed up to 800 °C is $ZnTiO_3$ although very small fraction of Zn_2TiO_4 and TiO_2 phases are partly coexisted. Furthermore, both the crystallization and decomposition temperatures of $ZnTiO_3$ phase seemed to be similar or somewhat lower compared to those in the sol–gel synthesis. Such experimental result means that as similarly to the sol–gel derived nano-crystal system [8, 11], the chemical reactions in ZnO–TiO_2 thin film system proceeded with relatively lower activation energy, probably by enhanced reaction properties, compared to the solid state reaction. Nevertheless, the reaction process in this thin film seemed to be more continuous and somewhat unclear rather than that of sol–gel process, due to the characteristics of thin film [15]. When AES depth profiling for zinc and titanium elements was examined, the composition of the prepared film was found to be uniform and almost unchanged along to the whole range of film thickness, compared to that before annealing. Figure 3 shows the AFM images of the thin films annealed at various temperatures. As the annealing temperature increased, the microscopic crystal particles of the film grew up slightly, due to the enhanced diffusion and condensation between particles. However, the surface morphology of the thin film annealed at 800 °C turned to be irregular and rough. It was confirmed by their comparing root mean square (rms) roughness values as shown in Fig. 4. The rms values were almost below ~4 nm for the films annealed up to 650 °C, and largely increased to ~10 nm for 800 °C. The dielectric properties of thin film annealed at various temperatures are

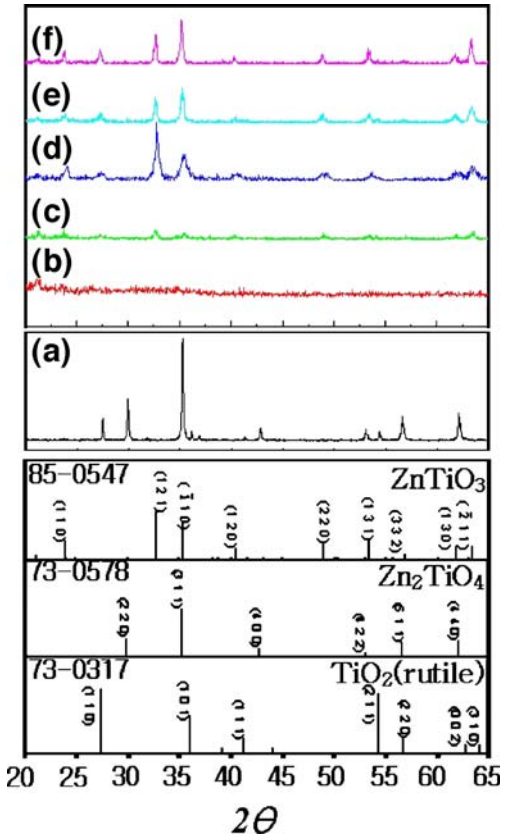

Fig. 1 XRD patterns of zinc titanate ceramic target (**a**) and thin films annealed at 500 °C, 2 h (**b**), 500 °C, 4 h (**c**), 600 °C, 2 h (**d**), 650 °C, 2 h (**e**) and 800 °C, 2 h (**f**), respectively

shown in Fig. 5. Higher loss above 20% of the as deposited (no annealed) film was effectively lowered by annealing. Dielectric constant and loss of the thin film annealed at 300 °C were 32 and 0.02 at 1 MHz, respectively. With increasing annealing temperature, the dielectric constant gradually increased and also dielectric loss was remained stable, below 1.7%. The maximum room temperature dielectric constant of 36–37 was obtained for the films annealed at 600–650 °C. The values seem to be so comparable to those of other bulk studies [8, 9]. Such increasing tendency could be explained in terms of phases present and surface morphology. The phase diagram of $ZnO–TiO_2$ system has represented that the phase of Zn_2TiO_4 and TiO_2 decomposed on heating above 945 °C in case of ZnO/TiO_2=1:1 [1]. And similar decomposition phenomenon at 800–1000 °C has been reported in the various ceramic powder system [2, 6, 9, 10]. Among them, Kim et al. [9] have demonstrated that in the microwave dielectric $(Zn_{1-X}Mg_X)TiO_3$ ceramics, the reason of higher dielectric constant over 20% at x=0 with increasing sintering temperature up to 950–975 °C, compared with 900 °C, is attributed to the appearance of TiO_2 (rutile) along decomposition on $ZnTiO_3$. As demonstrated by XRD patterns in Fig. 1, the $ZnTiO_3$ was detected as a major phase in the annealing condition of this study. While, the increase of annealing temperature induced the slight phase decomposition of $ZnTiO_3$, resulting in the appearance of Zn_2TiO_4 and weak rutile TiO_2. Considering the higher dielectric constant (k~105) of rutile phase compared to hexagonal $ZnTiO_3$ and cubic Zn_2TiO_4 phases [8], the increase of dielectric constant in this study was ascribed to the existence of rutile TiO_2. Furthermore, the uniform and well-grown morphology with annealing to 650 °C seems to assist the improvement in dielectric properties. These films showed nearly stable frequency dependency of capacitance within ±1% while dielectric loss was slightly increased with increasing frequency up to 5 MHz. When the annealing temperature was further increased to 800 °C, the dielectric response of the film became worse as shown in Fig. 5. Dielectric loss abruptly increased to 3.9% with decrease in dielectric constant, despite of nearly unchanged crystallinity in XRD pattern. The inferior dielectric properties could be understood in terms of degraded morphology of thin film due to excessive annealing temperature as confirmed by the data of Fig. 3(f) and Fig. 4.

4 Conclusions

Zinc titanate film with ~500 nm in thickness was fabricated by a RF magnetron sputtering using the ceramic target of ZnO/TiO_2=1:1 in composition. As-deposited amorphous

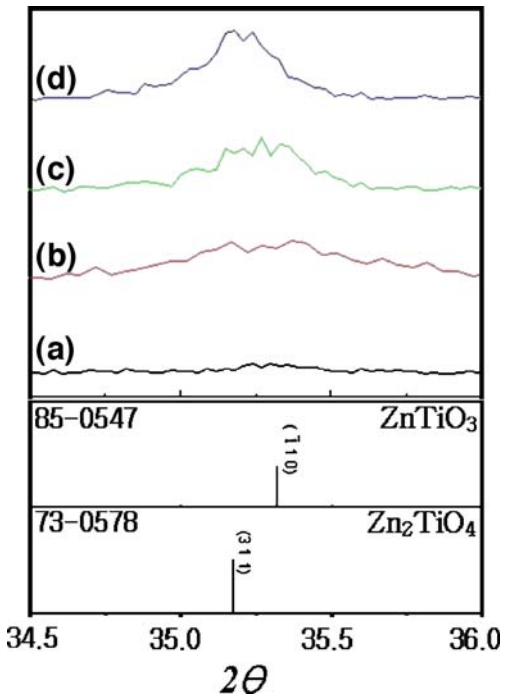

Fig. 2 XRD patterns in the 2θ ranges of 34.5°–36° with annealing temperatures of (**a**) 500 °C, (**b**) 600 °C, (**c**) 650 °C and (**d**) 800 °C, for zinc titanate thin films

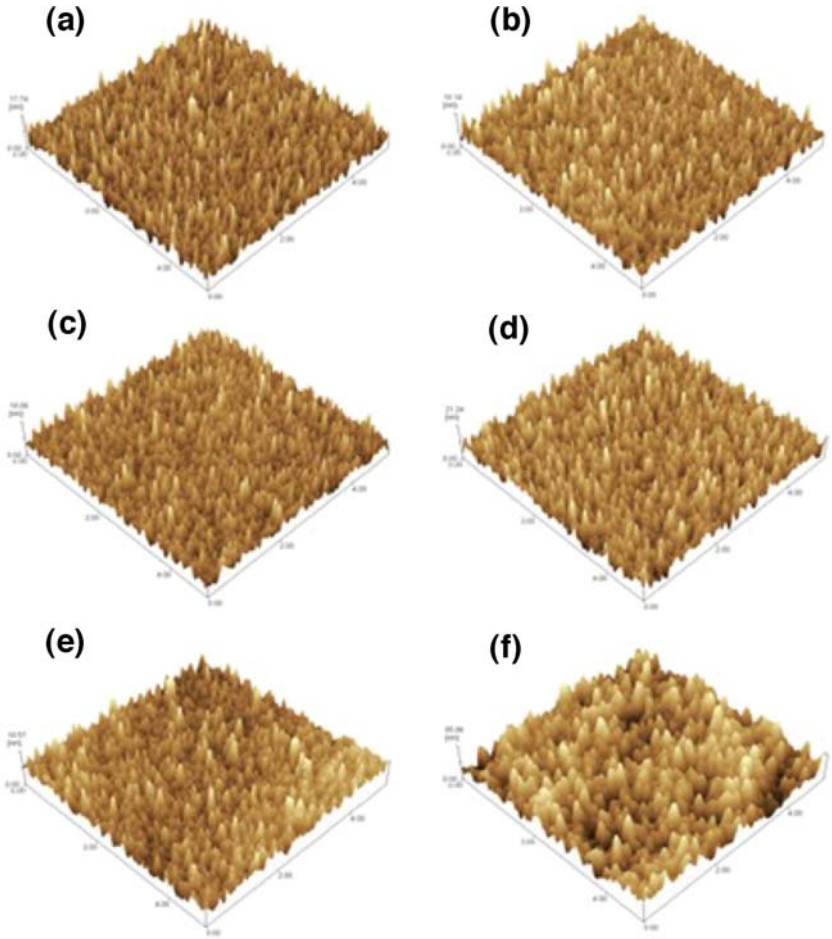

Fig. 3 AFM images of zinc titanate thin films as a function of annealing temperature; (**a**) no annealed, (**b**) 300 °C, (**c**) 500 °C, (**d**) 600 °C, (**e**) 650 °C and (**f**) 800 °C

film began to be crystallized into $ZnTiO_3$ phase at the annealing temperature of 500 °C. Dielectric constant increased and dielectric loss was somewhat decreased with increasing the annealing temperature up to 650 °C, where the values were about 36.8 and 1.7% at 1 MHz, respectively. It could be described that the presence of TiO_2 rutile phase created by the decomposition of $ZnTiO_3$ affected to the dielectric properties. The improved film morphology by the annealing up to 650 °C might also contribute to the enhancement of dielectric properties. The dielectric properties were, however, degraded with further higher annealing temperature of 800 °C, possibly due to the poor micro-

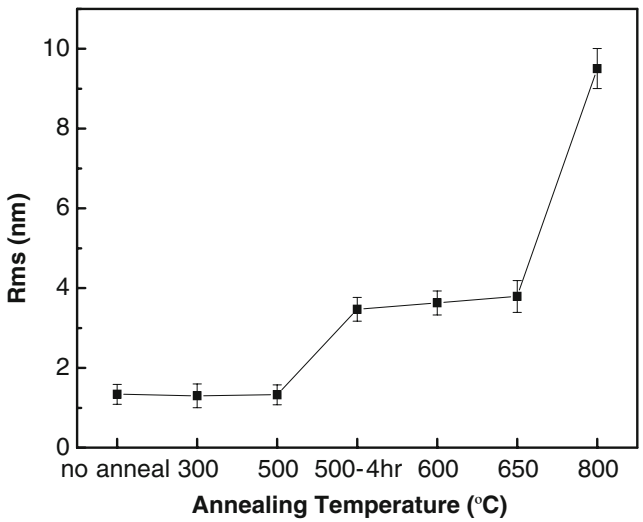

Fig. 4 Rms roughness values of zinc titanate thin films as a function of annealing temperature

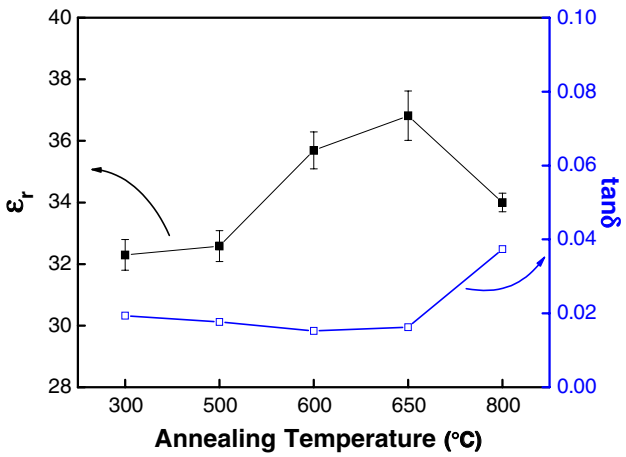

Fig. 5 Room temperature dielectric constant and loss of zinc titanate thin films as a function of annealing temperature (at 1 MHz)

structure of thin film. The dielectric response of zinc titanates thin films was considered to be critically dependent on phase nucleation and morphology varying annealing temperature.

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