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Crystallization and In-plane Alignment Behavior of $Pb(Zr,Ti)O_3$ Films

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Epitaxial $Pb(Zr,Ti)O_3$ (PZT) thin films were prepared on MgO(100) substrates by dipping-pyrolysis (DP) process using metal naphthenates as starting materials, and effects of pyrolysis and final heat-treatment conditions on the film's orientation were investigated Solid-state epitaxial growth of PZT proceeds at lower temperature around 650°C from the precursor pyrolyzed at 350 and 500°C. The in-plane alignment of the PZT films depends not only on the final heat-treatment temperature but on the pyrolysis conditions: the films, pyrolyzed at a higher temperature for a short time, i.e., at 500°C for 10 min, exhibited stronger orientation after the same final heat treatment at 650°~750°C The PZT films with the strongest orientation were prepared by pyrolysis under the above conditions followed by final heat treatment at 750°C.

Key words : $Pb(Zr,Ti)O_3$ thin films, MgO(100) substrates, Dipping-pyrolysis process, Solid-state epitaxial growth

I. Introduction

Recently, interest in the use of ferroelectric oxide thin films including $PbTiO_3$, $Pb(Zr,Ti)O_3$ and $(Pb,La)(Zr,Ti)O_3$ for applications such as microwave acoustic devices, dynamic random access memories (DRAMs), ferroelectric random access memories (FRAMs), and optical displays has increased greatly. For these applications it is preferable or essential to achieve a highly textured microstructure in thin films. The fabrication of PZT thin film is the subject of widely current interest as its unique properties offer many interesting device applications. The partial substitution of titanium by zirconium greatly influences the crystal structure of PZT; therefore, it is necessary to precisely control the composition of the films.

Various preparation methods have been reported for epitaxial growth of PZT thin films, including physical dry processes such as metalorganic chemical vapor deposition (MOCVD)[1,2] and rf-sputtering,[3] and chemical solution process such as sol-gel method.[4-6] A chemical solution process has advantages that it requires no high vacuum apparatus and is easily applicable to substrates with complicated shape and large surface. Metal naphthenates have the following advantages as compared with metal alkoxide: more simplicity of the process and stability in air to facilitate handling. But in so far as we know, there have been no reports on the preparation of "epitaxial" PZT thin films by DP process using metal naphthenates, although some papers have been published on the fabrication of epitaxial thin films by sol-gel method,[4-6] and polycrystalline PZT thin films by DP process.[7]

In this study, we report on the preparation of epitaxial PZT thin films on MgO single crystals (100) by DP process using metal naphthenates as starting materials. Since MgO, of which refractive index is lower than that of PZT and cost is relatively low, fabrication of epitaxial PZT films on MgO is attractive for application to optoelectric devices. Crystallinity and in-plane alignment of the product films were investigated.

II. Experimental Procedure

Figure 1 illustrates the representative processing scheme for synthesis of PZT films. A homogeneous coating solution having a molar ratio, Pb : Zr : Ti=1 : 0.52 : 0.48, was prepared by mixing of commercially available lead-, zirconium-, and titanium-naphthenates, and diluted with toluene to adjust the concentration and viscosity for depositing smooth films (concentration: 35.2 mg metal/ml coating solution). Excess Pb (5 mol%) was added to compensate volatilization during heat treatment. This solution was spin-coated (4000 rpm, 10 sec) onto MgO(100) substrates (20 mm × 20 mm × 1 mm^t).

The coated films were dried at 110°C for 30 min in air and pyrolyzed either at 200°C for 60 min (films A1-A4), at 350°C for 30 min (films B1-B4), or at 500°C for 10 min (films C1-C4) in air, in order to examine whether the crystallinity of product films is affected by the elimination mode of organic components.

The spin coating and pyrolysis were repeated five times to adjust the thickness of the precursor films. These pyrolyzed films were cut into pieces about the size

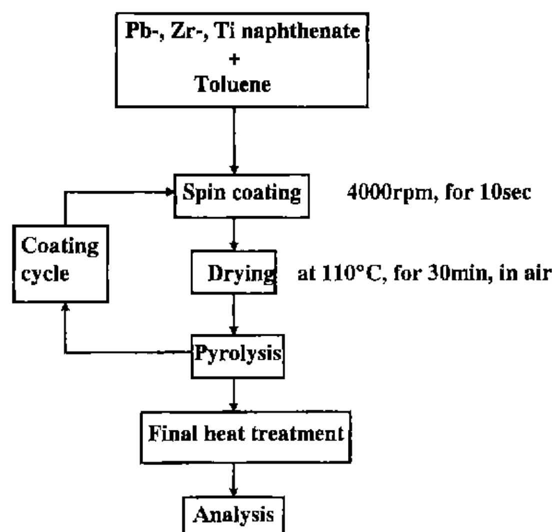

Fig. 1. Flow diagram of the PZT film preparation.

Table 1. Denotation of Resultant Films

Heat-treatment condition / Pyrolysis condition	600°C 30 min	650°C 30 min	700°C 30 min	750°C 30 min
200°C, 60 min	A1	A2	A3	A4
350°C, 30 min	B1	B2	B3	B4
500°C, 10 min	C1	C2	C3	C4

of 5 mm×5 mm and finally heat-treated at 600°~750°C for 30 min in air by directly inserting the samples into a preheated furnace, followed by fast cooling to room temperature. During the final heat treatment, the sample was placed on a platinum holder in a tube furnace. Final PZT films were denoted as A1-C4, as shown in Table 1.

The thickness of PZT films was ~0.6 μm, confirmed by observation of the fractured cross section of the films with scanning electron microscope (SEM) (JEOL JSH-5400). The films were examined by X-ray diffraction (XRD) θ-2θ scans and pole-figure analysis (β scans) (mac Science MXP[3A]) by the Schulz reflection method using CuKα radiation with a bent-crystal monochromator. Chemical composition was observed by SEM with energy-dispersive X-ray spectroscopy (EDS) (JED-2100) equipped with an ultra thin-film window (UTW) type X-ray detector.

III. Results and Discussion

1. Pyrolysis condition

After drying at 110°C for 24 h. the thermogravimetric - differential thermal analysis (TG-DTA) of the coating solution indicated that thermal decomposition and large weight loss of metal naphthenates mixture due to pyrolysis and combustion of organic components occurred

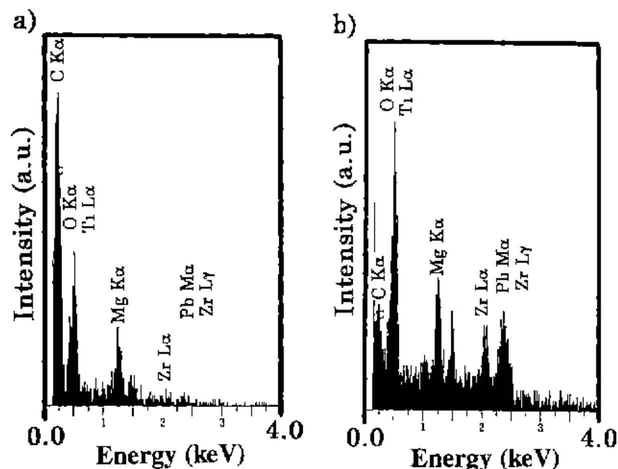

Fig. 2. EDS spectra of precursor films pyrolyzed at 200°C for 60 min (a) pyrolyzed at 500°C for 10 min and (b) respectively.

in the temperature range of 200° to 500°C. The results of TG-DTA showed that pyrolysis of starting metal naphthenates solution finished at 500°C. Thus, to investigate the effects of annealing paths during pyrolysis conditions of metal naphthenates, we prepared PZT films via the above mentioned prefiring conditions in experimental.

All the precursor films, pyrolyzed through three annealing paths, were found amorphous by XRD and smooth surfaces without cracks or voids by SEM observation and significant difference was not recognized among these films. There were differences, however, about the content of residual carbon or carbon hydroxides in the precursor films. Residual carbon content in the films was investigated by EDS. Figure 2 (a) and (b) shows EDS spectra of the precursor films pyrolyzed at 200°C for 60 min and at 500°C for 10 min, respectively. Comparing these two spectra, an apparent large peak of C-Kα was recognized in Fig 2 (a). It is difficult to obtain quantitative data of carbon content by SEM-EDS with a UTW detector if the sample is not bulk but thin film and carbon signal is also generated from carbon contamination during irradiation of electron beam. It is apparent, however, that precursor films pyrolyzed at 200°C for 60 min contained a larger amount of carbon than those pyrolyzed at 500°C for 10 min from the results of Fig. 2 (a) and (b). It should be noted that most of residual carbon, in precursor films pyrolyzed at 200°C for 60 min, had been eliminated in final PZT films. Figure 3 (a) and (b) shows EDS spectra of PZT films pyrolyzed at 200°C for 60 min (film A1), or at 500°C for 10 min (film C1), followed by final heat treatment at 600°C for 30 min. Figure 3 (a) and (b) gave similar spectra and there are no significant difference of residual carbon in final PZT films after the final heat-treatment at as low as 600°C between the two pyrolysis conditions.

2. XRD θ-2θ scans

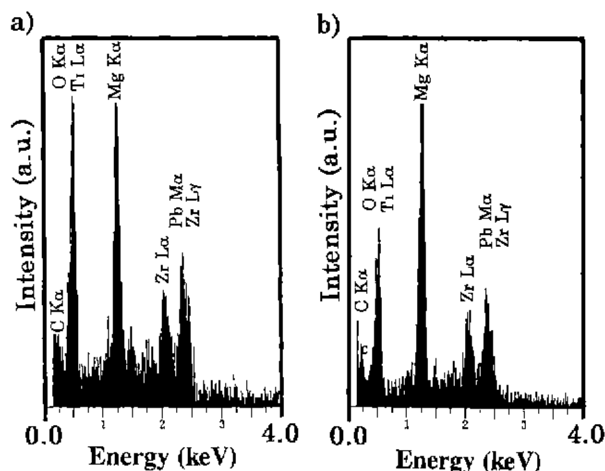

Fig. 3. EDS spectra of PZT films pyrolyzed at 200°C for 60 min (a) pyrolyzed at 500°C for 10 min and (b) followed by heat-treatment at 600°C for 30 min.

Figure 4 shows XRD θ-2θ scans of the product films pyrolyzed at 200°C (a), 350°C (b) and 500°C (c), followed by final heat treatment at various temperature. The (001) oriented perovskite PZT thin films were obtained by final heat treatment at 650°C and higher, and no evidence of misoriented peaks such as (110) or metastable pyrochlore phase was observed. Films A1, B1 and C1 were found to be amorphous. When the pyrolysis temperature was low, crystallization of PZT films was very difficult to occur; the resultant PZT film A2 was found to be almost amorphous and traces of PZT peaks were observed. By contrast, in the films B2 and C2 (Fig. 4 (b) and (c)) distinct (001) and (002) peaks of PZT were recognized. With increasing the heat-treatment temperature to 700° and 750°C, strong peaks were seen. For a stress-free, polycrystalline PZT ceramics, the (100) diffraction peak should be approximately twice as large as the (001) diffraction peak. We surmise that compressive film stress, chiefly owing to the thermal expansion mismatch between the PZT film (thermal expansion coefficient: 7.5 ppm/°C) and MgO substrate (14.5 ppm/°C), causes preferential c-axis alignment upon fast cooling across the Curie temperature. It should be noted that the peak intensity of PZT films was significantly affected by pyrolysis temperature although the final heat treatment temperature was the same. The lower peak intensity of resultant films shown in Fig. 4 (a) may be attributed to the presence of residual organic components. The above results of EDS of pyrolyzed films indicated that the PZT thin films pyrolysis at 200°C are assumed to contain some residual carbon or carbon hydroxides. In this case, crystallization of film and decomposition of organic components concurrently proceeded during final heat treatment. Crystal growth may be suppressed by residual carbon during the final heat treatment, resulting in the lower peak intensity of PZT films A1 and A2. When the films were heat treated at 700°C and higher, however,

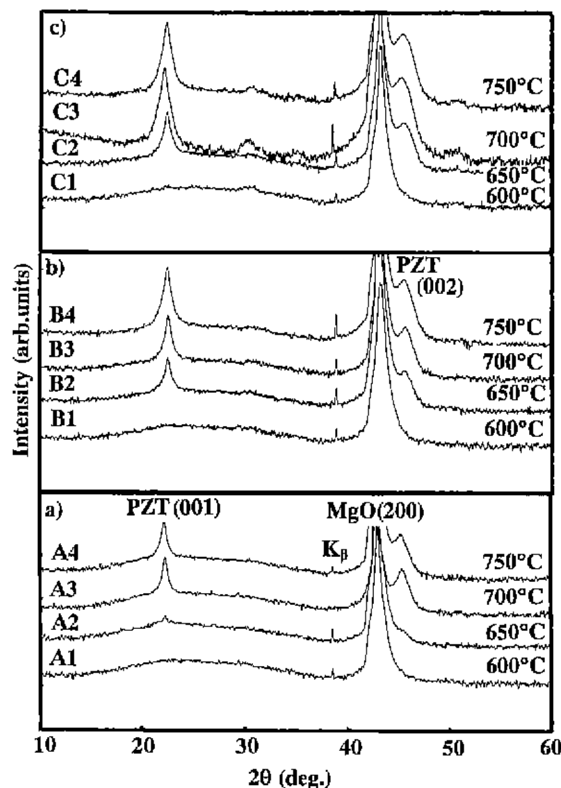

Fig. 4. XRD θ-2θ scans of PZT thin films A1-A4 (a) B1-B4, (b) C1-C4 and (c) on MgO (100) substrates.

strong (001) and (002) peaks were observed. For each pyrolysis condition, the higher the final heat treatment temperature the stronger the PZT (00l) peaks.

3. Pole-figure analysis

To further elucidate the orientation of the films, their in-plane alignment was investigated by X-ray pole figure analysis using the Schulz reflection method. In Fig. 5 is depicted the line profiles of β scans which correspond to α=45°. As clearly seen in Fig. 5, the shape of the line profiles was very sensitive to heat treatment and pyrolysis temperatures. Films A1, B1 and C1 gave only traces of the peaks beyond the noise level even if pyrolyzed at 500°C (film C1). In contrast, the β scan of the films heated at 700°C and higher exhibited four sharp peaks. Further, the β angles of these peaks were found to 45°-misoriented to the peaks of MgO(111) reflections. This means that these PZT films have grown epitaxially to the substrate surface. Moreover, the β scan profile of films A2-A4 exhibited four epitaxial peaks, but their intensities were considerably lower than those of films C2-C4. These results indicate that epitaxial growth of PZT films on MgO substrate requires higher temperature pyrolysis or a long holding time if the pyrolysis temperature is lower.

In Fig. 6 shows the (110) pole-figure of film C4. After setting 2θ=at 31.61° which corresponds to PZT(110)/(101) reflection, the film was rotated from β=0 to 360° at tilted

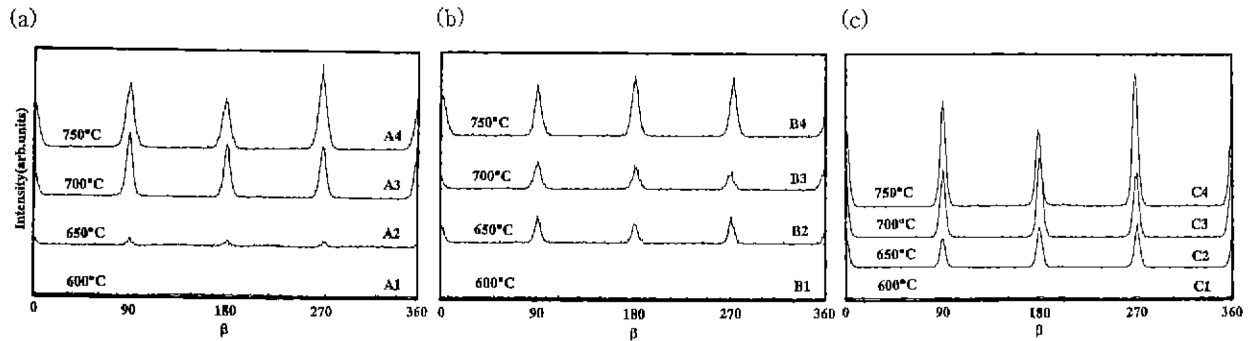

Fig. 5. Line profiles of β scans of PZT (110)/(101) reflection for films A1-A4 (a) B1-B4 and (b) C1-C4 (c).

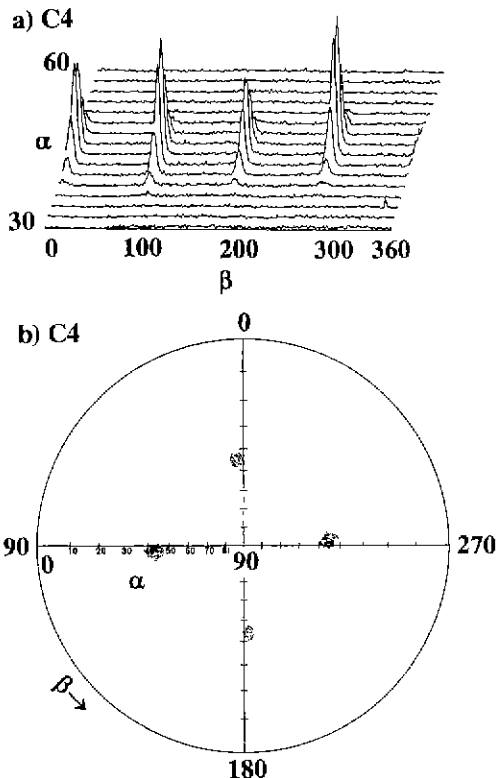

Fig. 6. X-ray pole figure of PZT (110)/(101) reflection for film C4: azimuthal (β) scans between 30° and 60° (a) and pole figure (b).

angles between α=30° to 60°. Four sharp spots were clearly recognized and the full widths at half maximum (FWHM) of film was 6.17°. This means that the PZT thin films have an epitaxial relationship with the MgO substrate.

Further investigation is in progress to optimize the holding time of low temperature pyrolysis to improve the epitaxy of thin films.

IV. Conclusion

Highly oriented PZT thin films were prepared on MgO single crystal (100) substrates by DP process using lead-, zirconium-, titanium naphthenates as starting materials. Crystallinity of PZT films depends on final heat treatment temperature as well as pyrolysis temperature. Epitaxially grown PZT films were obtained by pyrolysis at 200°, 350° and 500°C, followed by final heat treatment at 700° and 750°C. The X-ray pole figure analysis of PZT (110) plane indicated that the thin films have an epitaxial relationship with the MgO substrates.

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