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# Epitaxial Growth of $Pb(Zr, Ti)O_3$ Thin Films on $LaAlO_3$ Substrates by Dipping-Pyrolysis Process

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Epitaxially grown $Pb(Zr, Ti)O_3$ thin films were prepared on $LaAlO_3$ substrates by the dipping-pyrolysis process using metal naphthenates as starting materials. Homogeneous Pb-Zr-Ti solutions with toluene were spin-coated onto the substrates and pyrolyzed at 500°C. Highly oriented $Pb(Zr, Ti)O_3$ films confirmed by X-ray diffraction $\theta$-$2\theta$ scans were obtained by heat-treated at 750°C in air. The X-ray pole-figure analysis and reciprocal-space mapping of the resulting 0.6 μm films showed that the thin films comprising the *c*-axis oriented tetragonal phase have an epitaxial relationship with the $LaAlO_3$ substrates.

***Key words :*** Dipping-pyrolysis process, Metal naphthenates, Epitaxial relationship

## I. Introduction

In recent years, there has been an increasing interest in preparation of ferroelectric thin films in electronic devices such as microwave acoustic devices, infrared imagers, integrated optic circuits, optical displays and high-performance semiconductor memories. Solid-solution system of $PbZrO_3 - PbTiO_3$ (PZT) exhibit various properties, i.e., large permittivities, pyroelectricity and piezoelectricity.

Epitaxially grown thin films are more suitable for applications in various devices owing to their potential usefulness and stability. Consequently, the unique properties of this material have stimulated research in the development of physical and chemical processes for high-quality epitaxial PZT thin films.

Many methods have been employed for the growth of epitaxial ferroelectric thin films of PZT such as rf sputtering,[1] metalorganic chemical vapor deposition (MOCVD),[2,3] pulsed laser deposition (PLD),[4] and sol-gel method,[5,6] on various substrates, e.g., $SrTiO_3$,[7] MgO,[8] $SrBi_2Nb_2O_9$ (SBN),[8] and sapphire.[9]

Dipping-pyrolysis (DP) process is a wet chemical method that needs no high vacuum and is easily applicable to substrate with any shape and size; therefore, this is considered to be one of the most flexible and commercially promising technique for preparation of larger scale and high quality epitaxial thin films.[10-12] But so far as we know, there have been few reports on the preparation of epitaxial PZT thin films by DP process, although some papers have been published on the fabrication of polycrystalline PZT thin films.[13]

In this paper, we report on the preparation of epitaxial PZT thin films on $LaAlO_3$ (100), pseudocubic indice, (LAO) substrates by DP process with metal naphthenates used as starting materials. Crystal structure and in-plane alignment of the annealed films were investigated.

## II. Experimental Procedure

PZT thin films were prepared by a similar procedure presented in previous papers.[14,15] Briefly, homogeneous coating solution was prepared by mixing of commercially available lead-, zirconium- and titanium-naphthenate. This coating solution was diluted with toluene to an appropriate concentration and viscosity (concentration: 35.2 mg metal/ml coating solution). The molar ratio of the solution was set as $Pb : Zr : Ti = 1 : 0.52 : 0.48$, which corresponds to the morphotropic phase boundary (MPB) composition. Excess Pb (5 mol%) was added in the starting solution to compensate for vaporization loss of Pb during the final heat treatment.

The substrate used here was LAO (100) single crystal. LAO has a distorted perovskite structure at room temperature, which undergoes a structural phase transition from the rhombohedral to the cubic phase at 435°C.[16] Coating solution was spin-coated (4000 rpm, 10 s) onto successively cleaned substrate and pyrolyzed at 500°C in air for 10 min. The spin coating and pyrolysis procedure were performed five times for adjustment of the thickness of the pyrolyzed films. These pyrolyzed films were cut into pieces and subsequently heat-treated at 750°C in air for 30 min, then rapidly cooled down to room temperature.

The crystallinity and in-plane alignment of the films having thickness about ~0.6 μm, conformed by observation of fracture cross section of the films with a

scanning electron microscope (SEM), were examined by X-ray diffraction (XRD) θ-2θ scanning, and X-ray pole-figure analysis (β scanning) and reciprocal-space mapping[17] by the Schulz method using CuKα radiation.

## III. Results and Discussion

### *1. θ-2θ scans*

Figure 1 shows the XRD θ-2θ scans of the precursor films pyrolyzed at 500°C and of the final film heat-treated at 750°C, respectively The precursor film was amorphous, and strong PZT peaks which correspond to *a*- or *c*-axis orientation to the substrates were observed after heat treatments at 750°C. The tetragonal (110) reflection, corresponding to the strongest peak in PZT powder diffraction or non-oriented PZT grains, and other phases such as the pyrochlore phase were not detected in the final heat-treated film. The lattice constant ($d_{\perp}$) of this PZT film perpendicular to the substrate surface for film heat-treated at 750°C were determined to be $0.406_3$ nm, using LAO (200) peak as an internal calibration standard. This value ranged between the $a_0$ and $c_0$ values of bulk tetragonal PZT.

### *2. Pole-figure analysis*

The in-plane alignment of this film was determined by XRD pole-figure analysis using the Schulz reflection method. PZT (110)/(101) reflection was chosen for their intensity and separability from LAO reflections. After setting 2θ at 31.61° which corresponds to PZT (110)/(101) reflection, the film was rotated from β=0° to 360° at the tilted angles between α=30° and 60°. As shown in Fig. 2, the four sharp spots of PZT (110)/(101) reflections were observed at every 90° and the β angles of these spots

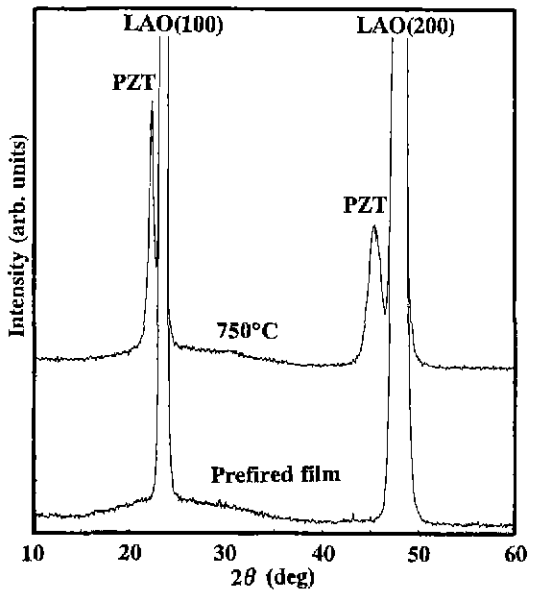


**Fig. 1.** XRD θ-2θ scans of PZT thin films coated an LAO (100) substrates.

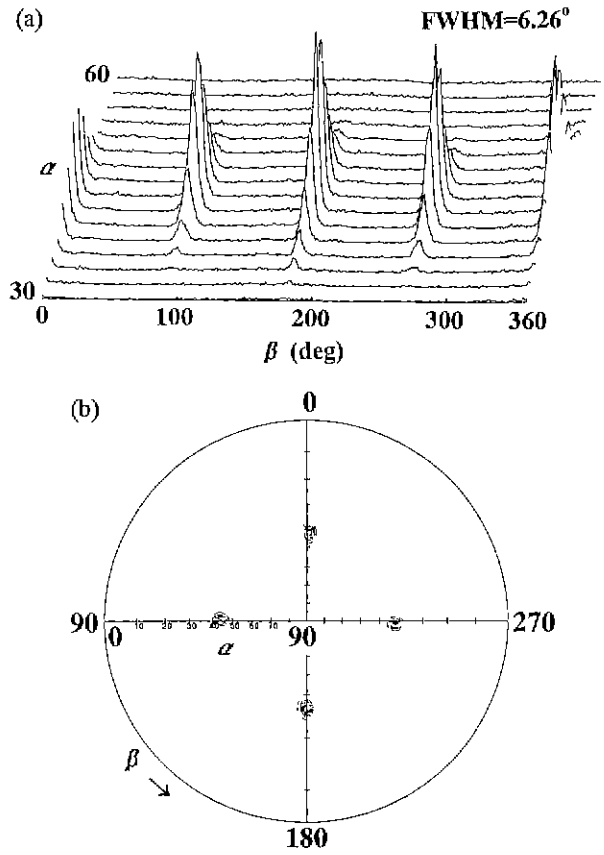


**Fig. 2.** X-ray pole-figure of (110)/(101) reflection for film annealed at 750°C: azimuthal (β) scans between 30° and 60° (a), and pole figure (b).

agreed with those for LAO (110) reflection not shown here. The full-widths at half maximum (FWHM) of the peaks along β direction were 6.26°. The comparison of these peak positions with those for the LAO substrate indicates an epitaxial relationship between PZT and LAO in which PZT [100] aligns with both [001] and [010] directions of the LAO substrate.

### *3. Reciprocal space mapping*

Further, to evaluate crystal structure and the lattice constants along the in-plane directions of the PZT films on LAO substrate, reciprocal-space mapping was measured for the film heat-treated at 750°C by asymmetric XRD 2θ/ω scans. In this paper, the θ- and ω-angles refer to symmetric and asymmetric Bragg reflections, respectively; their rotation axes are the same. Figures 3(a) and 3(b) show a bird's eye view and a contour, respectively, of the resulting 2θ/ω maps. A strong peak derived from the substrate of LAO (330) reflection at 2θ=119.3° and a small peak derived from the PZT (303) reflection of the epitaxial film at 2θ=109.1° are recognized in these mapping graphs.

We discussed the alignment of epitaxial PZT grains on the Nb-doped $SrTiO_3$(100) (STO) substrate, together with the corresponding reciprocal-space maps, in previous re-

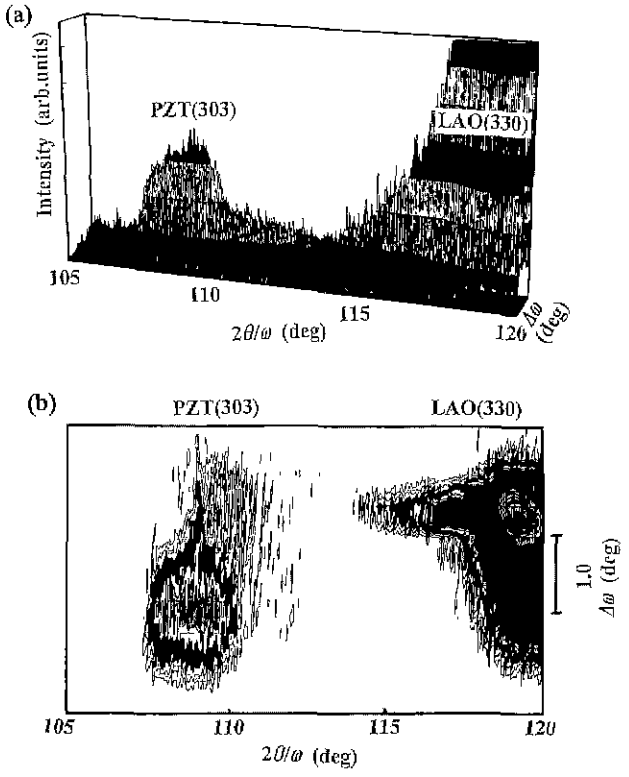


**Fig. 3.** A bird's eye view (a) and a contour (b) of XRD reciprocal-space (ω-2θ versus Δω) mapping around the LAO (330) reflection for film annealed at 750°C.

port.[14] From the results of PZT films on STO, if the PZT phase has a cubic or pseudo-cubic structure, only one spot corresponding to PZT (330) should appear on the same horizontal line of Δω as that of STO (330) and if the PZT is in the *c*-axis-oriented tetragonal phase, only one spot is expected to occur below the horizontal line of Δω which runs through that of STO (330). In our present results, only one spot corresponding to PZT appeared on below the horizontal line of Δω which runs through that of LAO (330), as seen in Fig 3(b). Therefore, the relative locations of the two spots corresponding to PZT (303) and LAO (330), indicating the *c*-axis orientation.

From the lattice constant $d_{\perp}=0.406_3$ nm calculated earlier by XRD θ-2θ scans and the position of peak top of PZT (303) and LAO (330), the lattice constant ($d_{//}$) of the PZT film along one of the in-plane directions was calculated to be 0.398 nm. Table 1 summarizes the lattice constants of the bulk tetragonal PZT, a PZT thin film prepared and LAO substrates used in this study. The $d_{\perp}$ (=$0.406_3$ nm) and $d_{//}$ (=0.398 nm) values of thin film are smaller than those of bulk tetragonal PZT. On the contrary, tetragonality is maintained, i.e., the $d_{\perp}/d$ ratio of thin film was 1.02, which is closer the $c_0/a_0$ (1.027) of the bulk tetragonal PZT. Thus our films are considered to be epitaxially grown *c*-axis oriented tetragonal PZT films. Furthermore, Tabata *et al.*[18] reported almost 100% *c*-axis-oriented $PbTiO_3$ films were formed at high cooling rate (~75°C/min). We also assume that the high cooling rate in the present experiment, i.e., around 200°C/min at 400°C, may favor the *c*-axis orientation.

**Table 1.** Comparison of Lattice Parameters

| Material | Structure | Lattice constant (nm) | Tetragonality |
|---|---|---|---|
| $LaAlO_3$ | Pseudocubic | $a_0=0.379$ | |
| $Pb(Zr_{0.52}Ti_{0.48})O_3$ (bulk) | Tetragonal | $a_0=0.403_6$<br>$c_0=0.414_6$ | 1.027 |
| $Pb(Zr_{0.52}Ti_{0.48})O_3$ (present film) | Tetragonal | $d_{//}=0.398$<br>$d_{\perp}=0.406_3$ | 1.02 |

It should be noted that FWHM of peaks along β direction is larger than that of PZT films on STO(100) substrates in previous work,[14] i.e., PZT/STO=2.4° and PZT/LAO=6.3°, while the crystal structure of resultant films are similar. Lattice mismatch between the *a*-axis of bulk PZT and STO is 5.8% and that of PZT and LAO is 8.5%. We assume that fluctuation of in-plane alignment of epitaxial PZT, based on the FWHM values along β direction in their pole figures, has a significant correlation with lattice misfit-values between film and substrates. In present work, PZT films on LAO exhibited a large FWHM value of 6.3° due to the larger misfit-value than that of films on STO.

## IV. Conclusions

Epitaxially grown PZT thin films were prepared on LAO single crystal (100) substrates by DP process with lead-, zirconium- and titanium naphthenates used as starting materials. Homogeneous Pb-Zr-Ti solutions with toluene were spin-coated onto the substrates and pyrolyzed at 500°C. Highly oriented PZT films confirmed by XRD θ-2θ scans were obtained by heat-treated at 750°C in air. The XRD pole-figure analysis and reciprocal-space mapping indicated that the thin films comprising the *c*-axis-oriented tetragonal phase have an epitaxial relationship with the LAO substrates.

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