

## Orientation Control of Low-Temperature Processed Pb(Zr,Ti)O<sub>3</sub> Thin Films

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Ferroelectric Pb(Zr,Ti)O<sub>3</sub> (PZT) thin films were deposited on Pt(111)/Ti/SiO<sub>2</sub>/Si substrate by a sol-gel method. PZT thin films were crystallized into perovskite single phase at temperature as low as 525°C by the addition of excess lead oxide of 20mol%. On the other hand, pre-annealing treatment affected the crystal orientation to form (111) and (100) oriented films with pre-annealing temperatures of 350°C and 420°C, respectively. The low-temperature processed PZT thin films with thickness about 400nm exhibited relatively good dielectric and ferroelectric properties at above 525°C. These electrical properties depended on the crystal orientation of the resultant films. Remanent polarization of (111)-oriented film annealed at 525°C was 46.1 μC/cm<sup>2</sup>, which is higher than that of the (100)-oriented one.

key words : Pb(Zr,Ti)O<sub>3</sub>, sol-gel, orientation, ferroelectric property, pre-annealing temperature

### 1. INTRODUCTION

Ferroelectric lead zirconate titanate, Pb(Zr, Ti)O<sub>3</sub>, so called PZT, thin films have been attracting wide interest due to their high potential for various applications such as in optical modulator, non-volatile semiconductor memories and in high-frequency surface acoustic wave (SAW) devices.<sup>1-3)</sup> PZT thin films are prepared by several techniques such as chemical vapor deposition, sputtering and wet chemical processing. Among them, a sol-gel method is one of the most promising techniques for processing high-performance ceramic thin films because it offers precise control of compositions on a molecular scale as well as a low processing temperature. However, a sophisticated sol-gel method is very hard to realize. An alkoxide route is the most expecting process for the idealized sol-gel. In this paper, ferroelectric PZT thin films were successfully deposited on a Pt/Ti/SiO<sub>2</sub>/Si substrate at low temperature though alkoxide route.

Ferroelectric PZT has a perovskite structure and therefore, PZT thin films with good ferroelectricity have a polarization axis, showing the different electrical properties depending on the crystal orientations of the resultant films. Consequently, orientation control is essential for the PZT films to apply various electronic devices with high performance. In some papers, preferred orientation and the orientation mechanism for the PZT thin films on Pt electrode were investigated. Brooks et al. explained film orientation with a viewpoint of phase transition rate of pyrochlore phase into perovskite phase which occurred during pre-annealing stage.<sup>4), 5)</sup> Chen et al. explained film orientation is ascribed to the difference of the phases that form at the interface between film and substrate.<sup>6), 7)</sup> Namely, PZT shows (111) orientation if the Pt<sub>3</sub>-Pb intermetallic compound is formed at the interface of film and substrate. On the other hand, PZT thin film shows (100) orientation when the PbO is formed at the interface. Tani et al. also reported that PLZT showed (111) orientation

when the Pt<sub>3</sub>Ti intermetallic compound existed on the substrate.<sup>9)</sup> Liu et al. suggested that PZT thin film had (111) orientation if the film was grown epitaxially, whereas the PZT film showed (100) orientation with a minimum surface energy when the heterogeneous nucleation occurred at the interface between film and substrate.<sup>9)</sup> Actually, Aoki et al. prepared (111) or (100)-oriented PZT films by a sol-gel method, which showed different electrical properties depending on the crystal orientation.<sup>10)</sup> However, these orientation control could be possible only though relatively high temperature process above 600°C. In the case of PZT thin film, low-temperature processing is very important because PZT thin films are expecting to use in a semiconductor process. High temperature processing will degrade a transistor on a silicon wafer and cause the migration of some elements during processing. In addition, various substrates with low-melting points such as metal aluminum and a transparent low-cost soda-lime glass could be available if the PZT films were deposited at lower temperatures, leading to the wide application of the ferroelectric PZT thin films. In the previous paper, perovskite PZT thin film with a relatively good dielectric property was prepared from the molecular-designed alkoxide precursor solution as well as by controlling the nucleation using seeding layers.<sup>11), 12)</sup> Takusagawa et al. also have synthesized almost single phase perovskite PZT thin film at 500°C.<sup>13)</sup> There are some papers on the low-temperature processing of PZT thin films.<sup>14), 15)</sup> However, these PZT films required high temperature annealing to obtain excellent electrical properties above 600°C.

This paper focuses on the orientation control of the low-temperature processed PZT thin films with excellent electrical properties. In this paper, relation between electrical properties and crystal orientation was also described. Crystal orientation of the resultant film was successfully controlled by the pre-annealing temperatures and the addition of a excess lead oxide. Addition of excess lead oxide will compensate the

depletion of a lead oxide due to evaporation and migration into the substrate during annealing. Excess lead oxide, which acts as a flux, is also expected to play an important role for the low-temperature processing.

## 2. EXPERIMENTAL PROCEDURE

Lead acetate trihydrate (Pb(OCOCH<sub>3</sub>)<sub>2</sub> · 3H<sub>2</sub>O), titanium iso-propoxide (Ti[(CH<sub>3</sub>)<sub>2</sub>-CHO]<sub>4</sub>), zirconium n-propoxide (Zr(OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub>) were used as raw materials. Anhydrous ethanol was used as a solvent. Lead acetate trihydrate was dehydrated and then dissolved into anhydrous ethanol by refluxing for 4 hours with ammonia gas flow to obtain Pb-precursor solution. On the other hand, Zr and Ti alkoxides solution were mixed to prepare the Zr-Ti alkoxide solution. This alkoxide solution was mixed and reacted with Pb-precursor solution to form molecular-designed 0.3M PZT precursor solution. Acetylacetone was added as a stabilizing agent of PZT precursor solution.

In this research, PZT precursor layers were deposited on Pt(111)/Ti/SiO<sub>2</sub>/Si substrate by dip-coating. The film thickness was about 400nm with 10 times of coatings. After each precursor layers were deposited, precursor films were pre-annealed in the range from 300°C to 420°C for 10 minutes in an air to pyrolyze the residual organic compounds from the precursor films. Finally, these amorphous precursor films were annealed at 500°C, 525°C, 550°C, or 600°C for 2 hours in an air.

In this paper, we prepared the PZT thin films with MPB composition and with 20mol% excess lead oxide composition. Each PZT thin film was abbreviated as PZT(100/53/47) and PZT(120/53/47), respectively.

The crystalline phases and orientation of the resultant PZT thin films were analyzed by X-ray diffraction (XRD). For electrical measurements, Au top electrodes with a diameter of 0.2mm were sputter-deposited. P-E hysteresis loops of the resultant films were measured by RT6600S (Radiant Technology Inc.).

## 3. RESULTS AND DISCUSSION

### 3.1 Effect of pre-annealing temperature and addition of excess lead oxide

Figure 1 shows the XRD patterns for the PZT(100/53/47) films pre-annealed at 350°C or 420°C and then annealed at 600°C. At 600°C, only a perovskite phase was identified. However, the crystal orientation of the resultant films depended on the pre-annealing temperature. PZT(100/53/47) film with a pre-annealing temperature of 350°C, where the residual organic compound in the film was pyrolyzed but the film was still amorphous, oriented in the (111) plane. On the other hand, pre-annealing at 420°C resulted in the partial crystallization and led to the (100) orientation of the resulting PZT(100/53/47) film annealed at 600°C. This suggests that the orientation of the resultant PZT(100/53/47) film could be successfully controlled by the pre-annealing temperature. Figure 2 shows the relation between crystal orientation and the pre-annealing temperatures for the PZT(100/53/47) film annealed at 600°C. Peak intensity ratio of the film was calculated

from the following equation;

$$\begin{aligned} (100) &: I_{(100)} / [I_{(100)} + I_{(110)} + I_{(111)}] \\ (110) &: I_{(110)} / [I_{(100)} + I_{(110)} + I_{(111)}] \\ (111) &: I_{(111)} / [I_{(100)} + I_{(110)} + I_{(111)}] \end{aligned}$$

Where  $I_{(hkl)}$  is the intensity of XRD pattern for (hkl) reflection. As a result, PZT(100/53/47) films annealed at 600°C exhibited strong (111) orientation if the films were pre-annealed below 350°C. On the other hand, pre-annealing above 400°C resulted in the strong (100) orientation of the resultant film. The factors that affect the crystal orientation of the thin film are the nucleation and the crystal growth. In this study, we assumed that the nucleation had large effect on the crystal orientation. The crystalline phases for the PZT(100/53/47) films annealed at 350°C or 420°C for 10 minutes were identified by XRD and shown in figure 3. From the figure, it was concluded that intermetallic compound of Pt<sub>5-7</sub>Pb(111) was identified clearly in the XRD pattern for the film pre-annealed at 350°C. In this case, the nearest

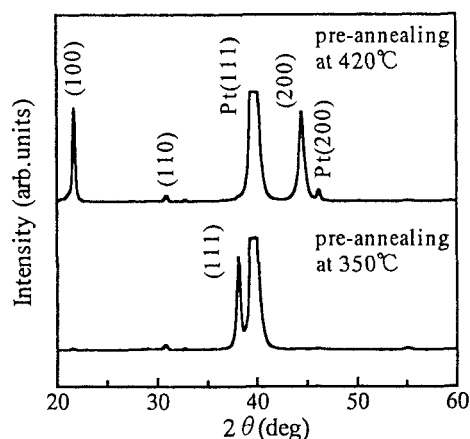


Fig.1 XRD patterns for PZT(100/53/47) thin films. The PZT films were annealed at 600°C by two processes.

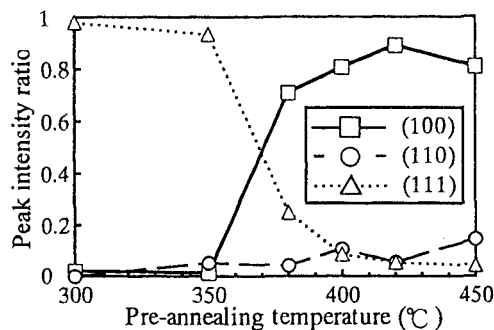


Fig.2 Graphical representation of XRD results showing orientation as a function of pre-annealing temperature for PZT(100/53/47) thin films annealed at 600°C.

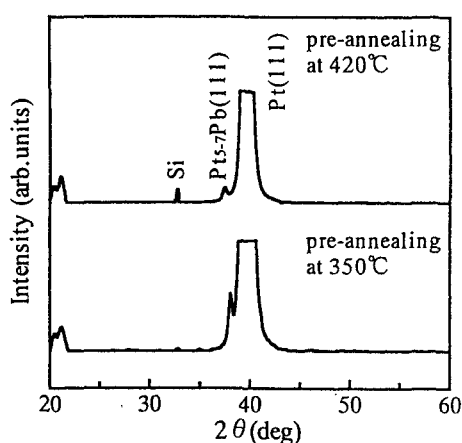


Fig.3 XRD patterns for PZT(100/53/47) thin films pre-annealed at 350°C or 420°C.

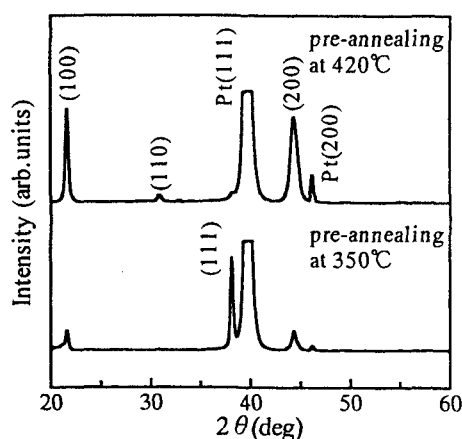


Fig.4 XRD patterns for PZT(120/53/47) thin films. The PZT films were annealed at 525°C by two processes.

neighboring interatomic spacing for (111) planes of Pt,  $Pt_{5.7}Pb$ , and PZT is 2.774 Å, 2.864 Å and 2.854~2.893 Å, respectively. It shows that each atom locates within 4% lattice mismatching. Therefore, it was concluded that intermetallic  $Pt_{5.7}Pb$  compound formed during pre-annealing at 350°C would reduce the interfacial energy between substrate and PZT(100/53/47) film, leading to the (111) orientation. On the other hand, weak  $Pt_{5.7}Pb(111)$  peak was confirmed in XRD pattern of PZT(100/53/47) film pre-annealed at 420°C. In this case, orientation mechanism is not clear. However, the heterogeneous nucleation would lead to the self-oriented growth of the (100) orientation that had minimum surface energy.

As described above, orientation control of the PZT(100/53/47) film is attained at above 600°C. However in this case, low-temperature processing is not possible because the pyrochlore phase with low dielectric property is still remained below 600°C. Therefore, the crystallization behavior of the PZT-(120/53/47) film was investigated. As shown in the figure 4, single phase perovskite films with different orientation were successfully deposited at 525°C by changing the pre-annealing temperature for the PZT

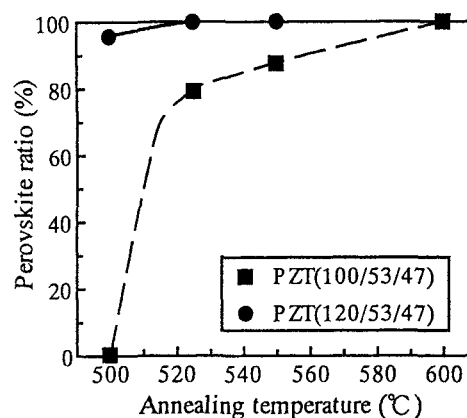


Fig.5 Relationship between annealing temperature and perovskite ratio. These thin films were derived from molecular-designed precursor solution.

system with 20mol% excess lead oxide addition. This shows that the excess addition of lead oxide lowers the conversion temperature of pyrochlore into perovskite phase. In addition, orientation of the low-temperature processed PZT(120/53/47) film was successfully controlled by the pre-annealing temperature. This also confirmed the orientation mechanism for the PZT film.

### 3.2 Relation between dielectric property and crystal orientation

The electrical properties of the PZT films are significantly affected by the residual pyrochlore phase and the crystal orientation of the resultant films. Figure 5 shows the change in the perovskite ratio for the PZT(100/53/47) and PZT(120/53/47) films pre-annealed at 350°C with annealing temperature. The perovskite ratio was calculated by the following equation;

$$\text{perovskite ratio(\%)} = I_{\text{max,perov}} / (I_{\text{max,perov}} + I_{\text{max,pyro}})$$

where  $I_{\text{max,perov}}$  and  $I_{\text{max,pyro}}$  indicate strongest XRD perovskite peak intensity and strongest XRD pyrochlore peak intensity, respectively. For the PZT(100/53/47) film, perovskite ratio increased with increasing annealing temperature and reached 100% at 600°C. Therefore, it is concluded that the seeding process is essential for the low-temperature processing of PZT(100/53/47) film. On the other hand, perovskite ratio for the PZT(120/53/47) film reached 100% at low temperature of 525°C, leading to the low-temperature processing. From this result, low-temperature processing of PZT(120/53/47) film with good ferroelectricity is expected. Therefore, the P-E hysteresis loops for the PZT(120/53/47) films with different pre-annealing temperatures or different crystal orientations were measured and shown in figure 6. As a result, remanent polarization( $P_r$ ) of (111)-oriented and (100)-oriented films were 46.1  $\mu\text{C}/\text{cm}^2$  and 21.7  $\mu\text{C}/\text{cm}^2$ , respectively. Figure 6 shows the well saturated hysteresis and relatively low coercive field of about 100kV/cm for both films, showing the good ferroelectricity. The difference of  $P_r$  for the resultant films was ascribed to the crystal symmetry of the resultant PZT(120/53/47) films.

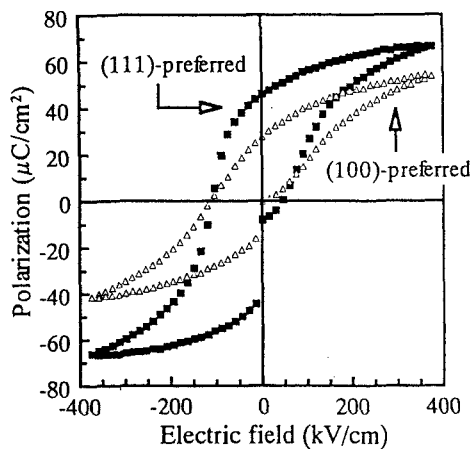


Fig.6 P-E hysteresis loops of PZT(120/53/47) thin films annealed at 525°C.

## CONCLUSIONS

This paper focused on the orientation of the low-temperature processed PZT thin films. Some parameters of pre-annealing temperature, annealing temperature and the addition of excess lead oxide in the precursor solution were changed to investigate the effects on the crystallization behavior and ferroelectric properties of the resultant films. As a result, followings are concluded;

- (1) A preferred orientation of sol-gel derived PZT thin films on Pt/Ti/SiO<sub>2</sub>/Si substrate was significantly affected by the pre-annealing temperature. (111)-oriented films were deposited with low pre-annealing temperature below 350°C, whereas the (100)-oriented films were obtained with relatively high pre-annealing temperature above 400°C.
- (2) Excessive addition of lead oxide is very effective for a low-temperature processing of PZT thin films. Single phase perovskite PZT films were successfully deposited at 525°C from precursor with 20mol% excess lead oxide.

(3) Highly oriented PZT thin films with good ferroelectricity were deposited as low as 525°C. The ferroelectricity of the low-temperature processed PZT films strongly depended on the crystal orientation of the resultant films.

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