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Growth mechanism of chemical solution derived PZT films on MgO(100) substrate

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PZT (Zr : Ti = 0.53 : 0.47) thin films were fabricated by chemical solution deposition with metal naphthenates used as starting materials. Effect of final annealing temperature on epitaxy and surface morphology of the films were investigated. PZT films prefired at 200°C were crystallized to be highly (00*l*)/(*h*00)-oriented at final annealing temperatures of 750°–800°C. The film annealed at 750°C was smooth and no distinct texture was exhibited, while the rosette-type microstructure caused by lead volatilization was observed in the films after annealing at 800°C.

1. Introduction

The solid solution system Pb(Zr, Ti)O_3 (PZT) is one of the best known ferroelectric ceramics that have the perovskite structure. Since the coupling factor and dielectric constant of PZT become highest at compositions around Zr : Ti = 1 : 1, the morphotropic phase boundary (MPB), these compositions are widely exploited in commercial preparations of PZT ceramics and films.

Thin films of PZT and related compounds are playing an important role as basic elements in a variety of solid-state devices, the major interest being in the non-volatile memories and actuators. In some applications, it is essential to prepare an oriented or epitaxial film with its polar axis perpendicular to the substrate surface.

Recently, epitaxial ferroelectric PZT films have been successfully grown by a number of deposition techniques such as chemical vapor deposition (CVD) [1, 2], rf sputtering [3, 4], pulsed excimer laser deposition [5] and sol-gel method [6, 7]. Among them, chemical solution depositions (CSD) such as sol-gel and dipping-pyrolysis (DP) processes offer inexpensive and versatile means as compared with the physical methods based on the complex apparatus.

CSD process is one of the most effective methods for the preparation of multicomponent oxide films, i.e., PZT and other ferroelectric films, because of the stability in air and easiness of handling as starting materials. However, in CSD, few reports on the epitaxial PZT films had been published until our previous papers [8–12] in which the preparation of epitaxial PZT thin films on various substrates were described. We demonstrated that the pyrolysis and final annealing temperature are quite effective for crystallization and epitaxy of films. In this paper, we investigated the effect of final annealing temperature on crystallinity and epitaxy of films, using films prefired at 200°C with which we had obtained epitaxial PZT films having homogeneous surface in the previous report [9].

2. Experimental

The experimental procedure and the reagents used in this study were almost the same as those on the previous reports [8–10]. Briefly, PZT sols (concentration : 35.2 mg metal/ml solution), which were derived from lead-, zirconium- and titanium-naphthenates in toluene, were used as precursors. The sol was diluted with toluene to adjust the concentration and viscosity for depositing smooth films. 5 mol% excess Pb was added to compensate volatilization during annealing. Thin films were coated onto cleaned MgO(100) single-crystal substrates by spinning the sol for 10 sec at 4000 rpm. Deposited films were dried at 110°C for 30 min and prefired at 200°C for 60 min in ambient atmosphere. This procedure was repeated five times before further annealing to achieve convenient thickness. After annealing, a thickness ∼0.6 μm was determined by observation of fractured cross section of the films with a scanning electron microscope (SEM). Films were crystallized at final annealing temperatures of 750–1000°C for 30 min in air by directly inserting the samples into a preheated tube furnace, followed by fast cooling to room temperature.

Films produced were characterized by X-ray diffraction (XRD) θ–2θ scans and pole-figure analysis (β scanning) by the Schulz reflection method. Morphology and chemical composition of PZT gel powder were investigated by SEM with an energy-dispersive X-ray spectrometer (EDS) equipped with an ultra thin-film window (UTW) type X-ray detector.

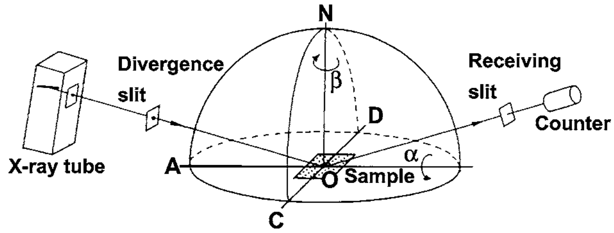

Figure 2 Schematic of XRD pole-figure measurement.

3. Results and discussion

In the previous work, the $(00l)/(h00)$-oriented perovskite films on MgO(100) substrates were obtained by final annealing at 650°C and higher [9]. In CSD for fabrication of PZT films, it has been found that the final annealing temperature was one of the most effective factors in determining the characteristics of the films. Therefore, in this report, the effect of final annealing temperature on the crystallinity, epitaxy and surface morphology of product films was examined.

Fig. 1 shows XRD θ–2θ scans of the produced films prefired at 200°C, followed by final annealing at 750–1000°C. Highly oriented PZT films were obtained by annealing at 750° and 800°C. It is easily seen that no evidence of misoriented or pyrochlore peaks were observed in these films. By contrast, with increasing the annealing temperature to 850°C and higher, the peak of $(00l)/(h00)$ was significantly broadened and disappeared, probably due to a stoichiometry deviation through the volatilization of lead species from the films during final annealing. In addition, at around 1000°C, ZrO_2 peaks such as (111) and (220) were observed.

In order to confirm the volatilization of lead species, relative Pb content to Zr and Ti in the PZT gel powders annealed at various temperatures for 30 min were investigated by EDS equipped with a UTW detector because it is difficult to identify the chemical composition of films exactly. Table I shows relative Pb content in PZT powder according to the annealing temperature. There is no significant difference in the Pb content between the powder pyrolyzed at 500°C for 10 min to eliminate organic component and powder annealed at 750°C. On the other hand, a small volatilization of Pb occurred at 800°C. Furthermore, with increasing the final annealing temperature to 850–1000°C, a large amount of Pb was vaporized. It is apparent that crystal growth may be suppressed by Pb volatilization during the higher annealing at 850–1000°C, resulting in lower peak intensity of PZT. It should be noted that the peak intensity of PZT films was significantly affected by the final annealing temperature. A strong peak intensity of highly oriented PZT was obtained by annealing at 750–800°C.

TABLE I Relative Pb ratio measured by EDS for PZT powder as a function of annealing temperature

	Temperature (°C)						
	500	750	800	850	900	950	1000
Pb ratio	1	0.98_6	0.95_0	0.92_5	0.93_6	0.89	0.90_3

[Pb ratio = $(Pb/Zr + Ti)_T/(Pb/Zr + Ti)_{500°C}$, T = temperature].

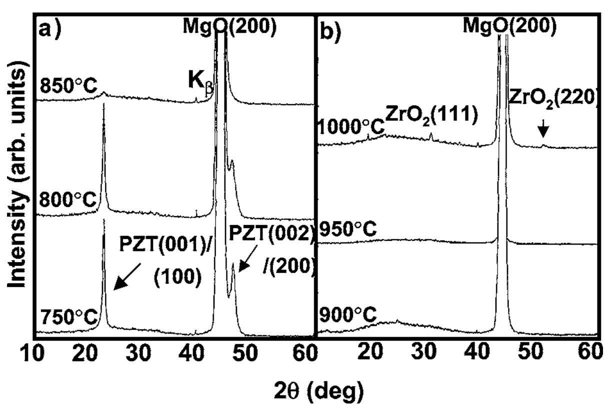

Figure 1 XRD θ–2θ scans of PZT films on MgO(100) substrates annealed at various temperatures.

The in-plane alignment of PZT$(00l)/(h00)$ texture on MgO(100) was further analyzed by X-ray pole-figure measurement. Fig. 2 illustrates the schematic of the method [13]. We used PZT(110)/(101) and MgO(111) reflections for this analysis since they are strong enough and there are no other interfering peaks around them. Briefly, at a fixed 2θ angle of 31.36° corresponding to the PZT(110) reflection [14], the sample was tilted by an α angle about the axis AB and rotated about the axis NO normal to the sample surface (angle β from 0° to 360°). If the PZT(001) films have a (pseudo) cubic structure, diffraction from the PZT(011) and its equivalent planes, i.e., (101), (011) and (101), will be successfully obtained with a 90° interval of β when the tilt α is 45°. The results of diffracted intensities versus β, or line profiles of β scans, for PZT films annealed at various temperatures are depicted in Fig. 3. As clearly seen in Fig. 3, variation of peak intensity was very similar with the above XRD θ–2θ results. The β scans of the films heated at 750° and 800°C exhibited four sharp peaks. The smaller the width of a peak, the greater the degree of texturing of the component corresponding to that peak, i.e., (001)/(100)

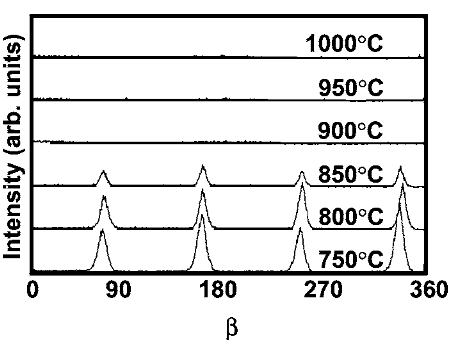

Figure 3 Line profiles of β scans of PZT(110)/(101) reflection for PZT films on MgO(100) annealed at various temperatures.

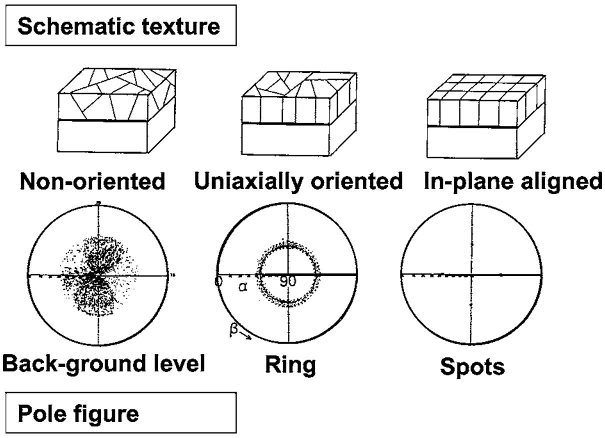

Figure 4 Grain alignment in films and pole-figures. Rings and spots indicate uniaxial orientation and in-plane alignment, respectively.

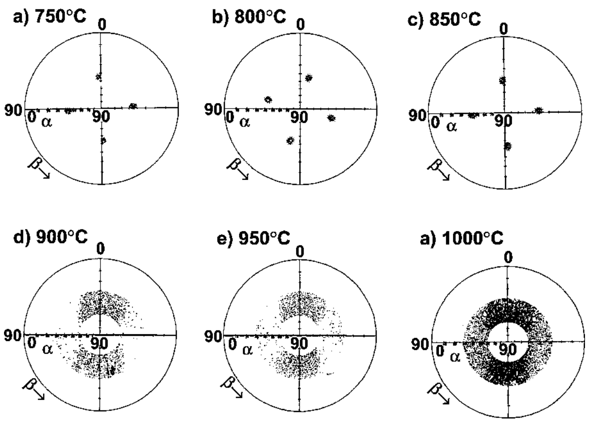

Figure 5 X-ray pole figures of PZT(110)/(101) reflection for PZT films on MgO(100) annealed at various temperatures.

orientation in this case. Similarly, β scans of MgO(100) substrates were measured at $2\theta = 36.98^\circ$ and $\alpha = 35^\circ$ using the MgO(111) reflections [Due to extinction rule, the MgO(110) reflection is absent]. The β angles of the peaks of MgO(111) were found to be 45° misoriented to the peaks of PZT(110)/(101) reflections. This means that these PZT films have grown epitaxially, i.e., cube on cube, to the substrates surface. In contrast, the films heated at 850°C and higher gave small peaks or only traces of the peaks beyond the noise level.

Moreover, the XRD pole-figures of PZT films were constructed using PZT(110) reflection. The pole-figures are made by plotting the diffracted intensity versus α and β in a circle (polar stereographic net) with β varying from 0° to 360° along the circumference and α varying from 0° to 90° along a radius from the circumference to the center of the circle (see Fig. 4) [13]. The intensity can be shown as contours in the circle, thereby indicating the sample orientations as a function of the combination of α and β angles. Thus, if the pole figure comprises spots at specified positions, some texture component, i.e., PZT(001), is bi-axially aligned, and if the figure is circular, this implies uniaxial orientation. In this work, four sharp spots were clearly recognized in the pole figures (see Fig. 5) for the films annealed at 750° and 800°C, which means that the PZT films have an epitaxial relationship with the MgO substrate, while a larger four spots or polycrystalline structure were exhibited in the films annealed at 850°C and higher. We assume that a stoichiometry deviation through a volatilization of lead species from the PZT film at high-temperature annealing as described in Table I, had effected on the epitaxial relationship between the films and substrates.

Fig. 6 shows the SEM images of surface morphology of PZT films annealed at various temperatures. It was found that for the film prepared at the optimum condition, i.e., though annealing at 750°C, the surface was smooth and no texture was observed as shown in Fig. 6a. On the other hand, the film annealed at 800°C as shown in Fig. 6b exhibited the rosette structure that is often seen in the microstructures of PZT films annealed at higher temperatures [15, 16]. The rosette structure is generally attributed to the perovskite PZT phase, whereas the fine-grained matrix is thought to consist of Pb-deficient pyrochlore phase, $PbTi_3O_7$ or $Pb_2Ti_2O_{6+x}$ [15, 16], although the XRD peaks

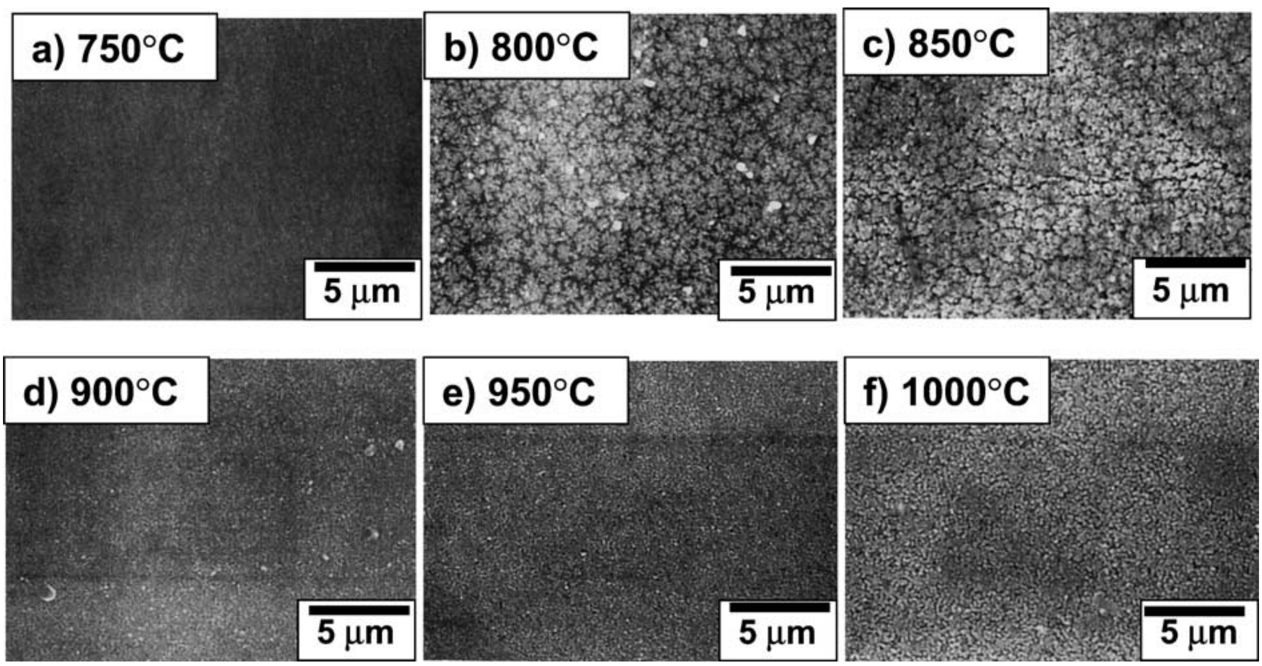

Figure 6 SEM photographs of the free surfaces of PZT films on MgO(100) annealed at various temperatures.

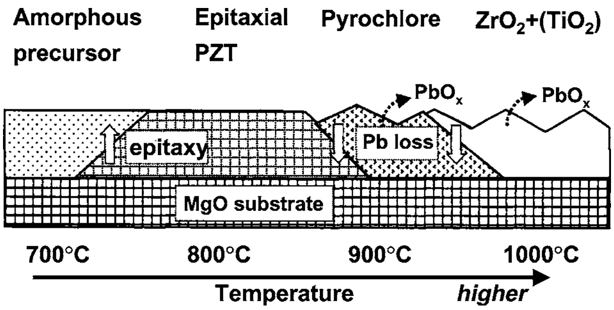

Figure 7 Growth mechanism of PZT films on MgO as a function of annealing temperature. Arrows in the film indicate the directions of growth of the specified phases.

corresponding to the pyrochlore were absent as shown in Fig. 1. Moreover, polycrystalline grain morphology with grain sizes of submicron order was observed in the films annealed at 850°C and higher, Figs 6c–f. Micropores interspersed among grains are most significant in the film annealed at 850°C, Fig. 6c. It is noted that the films annealed at 850°–950°C showed only traces of XRD peaks (see Fig. 1). This suggests that crystallinity of the films is quite low through decomposition of PZT or of the intermediate pyrochlore phase associated with Pb-volatilization. Kwok *et al.* [17] showed that surface composition of the sputter-deposited PZT films became Zr-rich as annealing temperature was raised or annealing time was increased. This is also the case for the present study since weak but distinct ZrO_2 peaks were recognized in the θ–2θ scans for the film annealed at 1000°C, in Fig. 1. Growth mechanism of PZT films obtained in this work is summarized in Fig. 7. From these results, it can be concluded that formation of highly oriented and uniform PZT films is possible by preventing lead deficiency during final annealing. However, it has not been clarified yet if 5 mol% excess Pb introduced any residual lead-oxide-rich phases in the films or was completely evaporated during final annealing. Further work is required to establish the precise control of excess Pb amount.

4. Conclusion

PZT thin films were fabricated by CSD with metal naphthenates used as starting materials. Effect of final annealing temperature on epitaxy and surface morphology of the films were investigated. PZT films prefired at 200°C were crystallized to be highly $(00l)/(h00)$-oriented at final annealing temperatures of 750°–800°C. The film annealed at 750°C was smooth and no distinct texture was exhibited, while the rosette-type microstructure caused by lead volatilization was observed in the films after annealing at 800°C.

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