

Preparation Condition of Lead Zirconate Titanate (PZT) Thin Film from Liquid Phase by Hydrothermal Electrodeposition

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$\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT) thin films have been grown on SrTiO_3 single crystal substrate (STO) with $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ conducting buffer layer (LSMO) by means of hydrothermal electrodeposition under various preparation conditions. In the experiment, the powders of $\text{Pb}(\text{OH})_2$, ZrOCl_2 , and TiO_2 (anatase) were added into KOH solution (6-10 M). After 24 h reaction at 90-110 °C, the (00 l) oriented PZT thin film with Zr content ($\text{Zr}/(\text{Zr}+\text{Ti})$) of 16-44% was grown on LSMO/STO substrate. From the SEM observation, the surface morphologies of films were classified into 3 groups, i.e., the film consisted of the small rectangular shaped crystallites (~100 nm, group A), larger crystallites (100~300 nm, group B), and flat rectangular crystallites (300 nm~, group C). The group A films preferred the high KOH concentration and the high reaction temperature, while the group C films were obtained from 6 M KOH solution irrespective of reaction temperature. The PZT (002) peak was observed at 44~44.5° in XRD for groups A and B films, while that appeared at 43.6° for group C films. For all of groups, the film growth was initiated from the deposition of fine grains of 10-20 nm in size.

Key words: Lead zirconate titanate, Epitaxial growth, Hydrothermal electrodeposition

1. INTRODUCTION

$\text{Pb}(\text{Zr}_x\text{Ti}_{1-x})\text{O}_3$ (PZT) is well known as excellent ferroelectric material and used as capacitor, DRAM, etc. in electronic industry. Thus, its physical properties [1,2] and synthesis methods [3-5] have been widely studied in relation to its ferroelectricity. For thin film device, it is necessary that the film maintains tetragonal structure and c -axis orientation. For this purpose, epitaxial growth of PZT film was reported by using hydrothermal method at 90-150 °C on SrTiO_3 or LaAlO_3 single crystal [6]. Recently, we have proposed a novel method for thin film synthesis, hydrothermal electrodeposition [7]. By using hydrothermal electrodeposition, the epitaxial thin film of BaTiO_3 [7], PbTiO_3 [8] were successfully grown on SrTiO_3 single crystal substrate (STO) with $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ conducting buffer layer (LSMO) at lower temperature of 60-110 °C. Further, it was found that the features of hydrothermal electrodeposition was the deposition of fine grains with a few tens nm in size.

In this paper, we tried to prepare the PZT thin films on SrTiO_3 single crystal substrate with LSMO buffer layer by using hydrothermal electrodeposition at 90-110 °C. The effects of preparation conditions (temperature and KOH concentration) on crystal structure, film composition, and film microstructure were investigated.

2. EXPERIMENTAL

$\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ thin film was spin-coated on (100) oriented SrTiO_3 single crystal substrate as conducting buffer layer. This is denoted as LSMO/STO hereinafter. $\text{Pb}(\text{OH})_2$, ZrOCl_2 , and TiO_2 were used as the starting materials for hydrothermal electrodeposition. Prior to the deposition, 0.645 g of ZrOCl_2 powder was added in 15 ml of KOH solution and kept for more than 48 h at 90-110 °C to be solved as much as possible. Then, the mixture of 1.5 g of $\text{Pb}(\text{OH})_2$ and 0.16 g of TiO_2 powder were added into the solution. LSMO/STO substrate and Pt counter electrode were suspended into the solution and the voltage of 1 V (direct current) was applied between electrodes (LSMO/STO : negative, Pt : positive) at 90-110 °C for 24 h. The detailed procedure is referred to our previous papers [7, 8].

The PZT films obtained were characterized by means of XRD (Philips X'pert, $\text{CuK}\alpha$ radiation), FE-SEM (Hitachi S-4300) and XPS (Perkin Elmer ESCA5000, $\text{Al K}\alpha$ radiation). The binding energies in XPS were referred to $\text{C}1s=285.0$ eV.

3. RESULTS AND DISCUSSION

Figure 1 shows the X-ray diffraction patterns of PZT thin films prepared on LSMO/STO single crystal substrate under various conditions by hydrothermal

electrodeposition. The PZT related diffraction peak was observed only in the range 43-45° and assigned to (002) of tetragonal PZT. Other than this peak, (200) peaks for cubic SrTiO₃ and pseudo-cubic La_{0.7}Sr_{0.3}MnO₃ appeared at 46.48° and 46.90°, respectively, in the range of 30-60°. This result means that the (00 l) oriented PZT film was grown on LSMO/STO substrate. From the JCPDS data [9], PbTiO₃ has tetragonal crystal structure with lattice constants of 0.3899 nm for a -axis and 0.4153 nm for c -axis, while tetragonal PbZr_{0.52}Ti_{0.48}O₃ has the lattice constants of 0.4036 nm (a -axis) and 0.4146 nm (c -axis). Although it is difficult to distinguish between PbTiO₃ and PZT from the XRD data, it was verified by XPS analysis that both Zr and Ti were contained in the film. Further, the crystallographic data indicates that the lattice constant for c -axis almost unchanged in the PZT film with Zr content less than 0.52. Since the lattice constant of a -axis for cubic SrTiO₃ is 0.3905 nm, the a -axis lattice constant of tetragonal PbZr_{0.48}Ti_{0.52}O₃ has good matching with that for SrTiO₃ substrate, causing the (00 l) orientation of PZT film. From Fig. 1, the (002) diffraction peaks appeared at 44.2-44.5° for the films prepared in 10 M KOH at 90-110 °C (Fig. 1 a-c). On the other hand, the peak was observed at 43.7° for the film prepared in 6 M KOH at 110 °C (Fig. 1 d). The peak position for latter film was well consistent

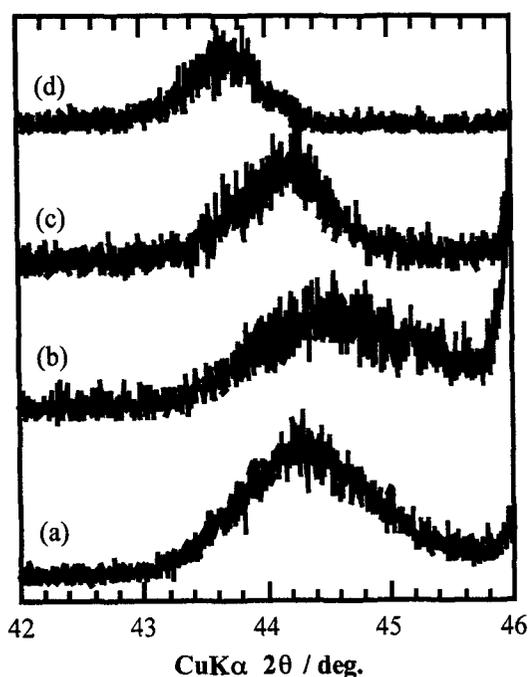


Fig. 1 X-ray diffraction patterns of PZT thin films prepared by hydrothermal electrodeposition in (a) 10 M KOH at 110 °C, (b) 10 M KOH at 100 °C, (c) 10 M KOH at 90 °C, and (d) 6 M KOH at 110 °C.

with the reference data, while that for the former was higher than the reference, suggesting the small lattice constant in the former film. The (002) peak positions for the films prepared under each condition were summarized in Table 1. The peak could not be observed for the film prepared in 6 M KOH at 90 °C because the film was too thin. The (002) peak appeared at higher degree (44.1-44.5°) for the PZT films prepared in 8-10 M KOH, while the (002) peak at 43.6-43.7° was observed for the film prepared in 6 M KOH. It seems that the KOH concentration strongly affects the (002) peak position, i.e., the crystal structure.

The film microstructures were observed by SEM and the films were classified into 3 groups (group A-C) concerning the surface morphology. Figure 2 shows the typical surface SEM images for the films belong to each group. The group A film, which was obtained in KOH with high concentration at high temperature, consisted of the stack of fine rectangular shaped grains (<100 nm). In the group B film, the larger rectangular grains of 150-250 nm in size as well as fine grains (~20 nm) were observed in the film. On the other hand, going to group C film, which was obtained in 6 M KOH irrespective of temperature, the large flat grains more than 500 nm in size grew on the substrate. The group B film was obtained under moderate condition, i.e., in 8-10 M KOH at lower temperature. The relationship between preparation condition and classification is summarized in Table 2. Comparing Tables 1 and 2, the crystal structure ((002) peak position) seems to relate to surface morphology. For the group C film, the (002) peak position was well consistent with the reference data (43.6°), while the position shifted to higher degree side for groups A and B films. The deviation from reference data increased in the order of C→B→A. Taking into account grain size in each group film, the larger grain has the same lattice constant as the reference, while the lattice constant of c -axis decreased with decreasing grain size.

The surface Zr-Ti compositions in PZT film prepared under various conditions were evaluated by XPS and the results are shown in Fig. 3 as a function of KOH concentration and deposition temperature. Zr

Table 1 (002) peak position for the film prepared under various conditions by hydrothermal electrodeposition.

Deposition temp. / °C	KOH concentration / M		
	10	8	6
110	44.3°	44.5°	43.7°
100	44.5°	44.2°	43.6°
90	44.2°	44.1°	-

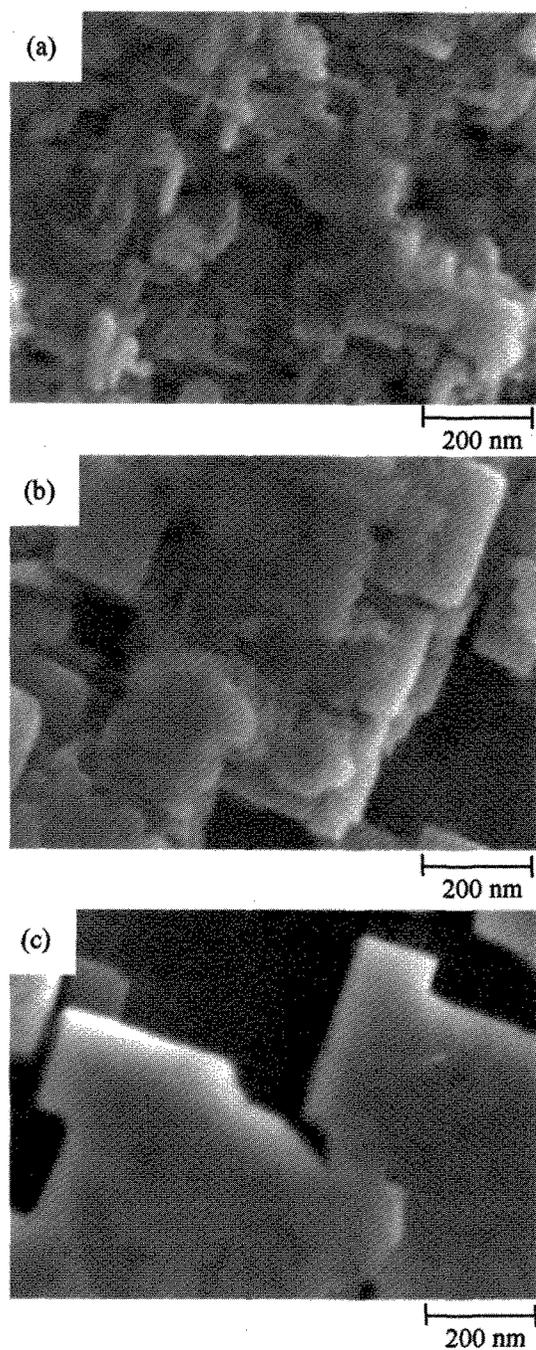


Fig. 2 Surface SEM images of PZT thin films prepared by hydrothermal electrodeposition in (a) 10 M KOH at 110 °C, (b) 8 M KOH at 100 °C, and (c) 6 M KOH at 110 °C.

Table 2 Classification of surface morphology for the films prepared under various conditions.

Deposition temp. / °C	KOH concentration / M		
	10	8	6
110	A	A	C
100	A	B	C
90	B	B	C

was included in all of films prepared under various conditions and the Zr concentration ($Zr/(Zr+Ti)$) ranged from 16% to 44%. The Zr concentration tended to increase with increasing KOH concentration and deposition temperature. However, the Zr concentration fluctuated under the same condition or the tendency was

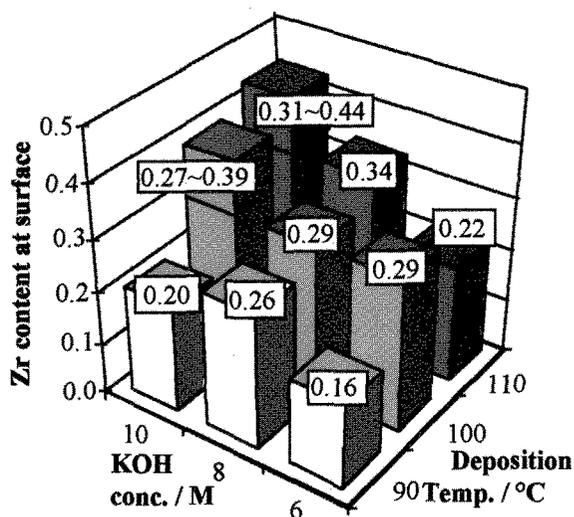


Fig. 3 Surface Zr content evaluated by XPS for PZT films as a function of KOH concentration and deposition temperature.

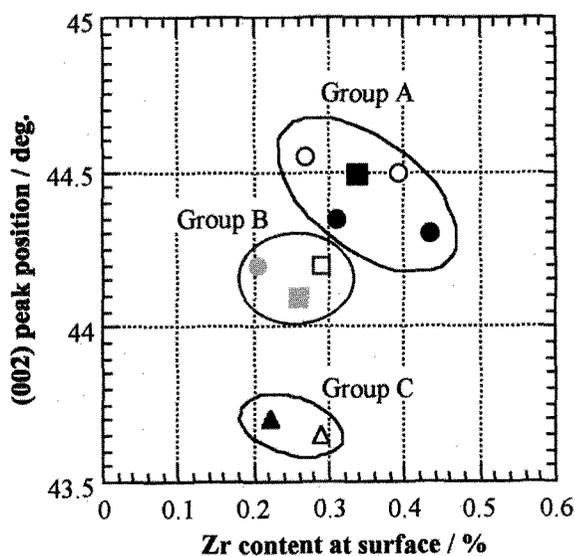


Fig. 4 Correlation between surface Zr content and (002) peak position for the PZT films prepared by hydrothermal electrodeposition.

● : 10 M KOH at 110 °C, ○ : 10 M KOH at 100 °C, ⊙ : 10 M KOH at 90 °C, ■ : 8 M KOH at 110 °C, □ : 8 M KOH at 100 °C, ⊞ : 8 M KOH at 90 °C, ▲ : 6 M KOH at 110 °C, and △ : 6 M KOH at 100 °C.

not monotonous. This suggests that the Zr concentration is difficult to be controlled by changing KOH concentration and deposition temperature. Figure 4 depicts the correlation between the surface Zr concentration and (002) peak position for the PZT films prepared by hydrothermal electrodeposition. The group name to which each plot belongs is also indicated in the figure. It is noted that the Zr concentration varies in each group in the range of 20-44%. In other words, the PZT films with different Zr content had the same lattice constant of *c*-axis. The *c*-axis lattice constant hardly changes between PbTiO_3 (Zr conc.=0%) and $\text{PbZr}_{0.52}\text{Ti}_{0.48}\text{O}_3$ (Zr conc.=52%). The Zr concentration range obtained in this paper is included in this range. Thus, the above findings are considered to be reasonable. On the other hand, the factor determines the crystal structure seems to be grain size. It is considered that the large flat grains in group C film apt to have bulk structure consistent with the reference, while the smaller grains in groups A and B are affected from the substrate to have smaller *c*-axis lattice constant due to the lattice distortion.

Finally, the growth mechanism of PZT film is

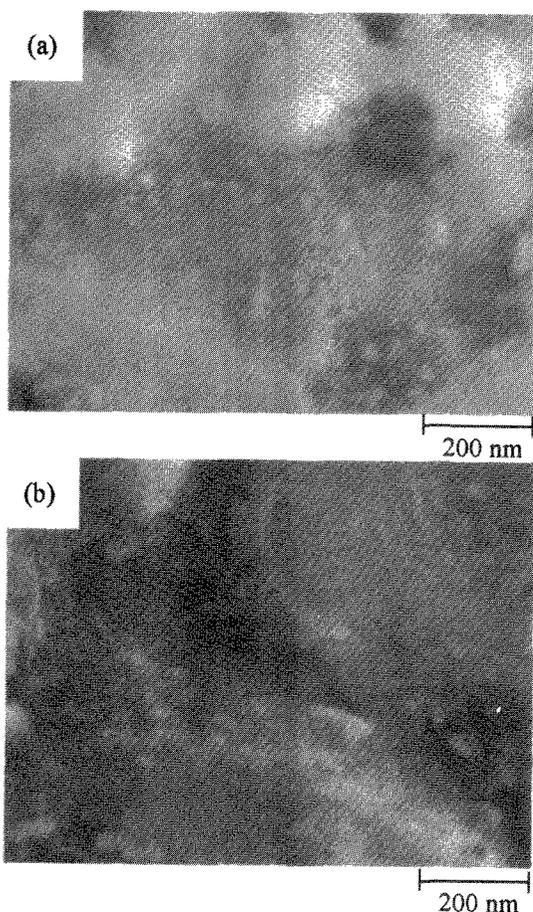


Fig. 5 Surface SEM images of PZT films in initial growth stage. (a) group A, (b) group C.

mentioned below. In this paper, the LSMO/STO substrate was perpendicularly suspended in KOH solution having the mixed powder of $\text{Pb}(\text{OH})_2$, ZrOCl_2 , and TiO_2 at the bottom of reaction vessel. Thus the film at the upper part was very thin and the thickness increased with going to the bottom part. This suggests that the film growth process can be understood from the observation of film microstructures from the upper to the bottom parts. Figure 5 shows the surface SEM images at upper part of substrate prepared in 10 M KOH at 110 °C (group A) and in 6 M KOH at 110 °C (group C). In both images, fine grains of ca. 10-20 nm in size were sporadically deposited on the substrate. This means that the initial stage of film growth is the same for the films in any groups, i.e., the film growth is initiated from the deposition of fine grains (10-20 nm). With increasing film thickness, the grains are stacked on the grains and the film consists of the small crystallites (group A), while the grains grow horizontally to become flat large crystallites (group C). It is assumed that the growth to perpendicular direction is preferred in group A, while that to horizontal direction is favored in group C. These differences of growth mode are controlled by the KOH concentration.

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