

Epitaxial Growth of Lead Titanate Thin Film by Hydrothermal Electrodeposition

Dai Matsushiro, Jun Tamaki, Yoshifumi Yamamoto, and Masao Matsuoka

Department of Applied Chemistry, Faculty of Science and Engineering, Ritsumeikan University,

Kusatsu-shi, Shiga 525-8577, Japan

Fax : 81-77-561-2659, e-mail : juntre@se.ritsume.ac.jp

The hydrothermal electrodeposition method has been used to prepare the epitaxially grown PbTiO_3 (PTO) thin film on single crystal SrTiO_3 substrate with $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ conducting buffer layer (LSMO/STO). The *c*-axis oriented PTO film was obtained at 90-110 °C after 24 h deposition. The thickness and thus the rate of film growth increased with increasing preparation temperature. At the early stage of growth, the film consisted of fine and cubic particles (ca. 20 nm) and they were epitaxially deposited on the LSMO/STO substrate. When the film was grown, the fine particles aggregated to form large crystallite. The growth mode of PTO thin film was compared under different preparation conditions.

Key words: Lead titanate, Epitaxial growth, Hydrothermal electrodeposition

1. INTRODUCTION

Ferroelectric perovskite oxides such as BaTiO_3 (BTO), PbTiO_3 (PTO) and $\text{PbZr}_x\text{Ti}_{1-x}\text{O}_3$ (PZT) are the most important materials in electrical industry. These have been used as capacitors, nonvolatile memories, and pyroelectric sensors [1]. Ferroelectricity is originated from their tetragonal crystal structure. The epitaxially grown film with *c*-axis orientation is preferred in order to obtain high dielectric constant. The hydrothermal synthesis of PTO was reported by Gelabert *et al.*, in which PTO powder was prepared from PbO and TiO_2 under hydrothermal condition at 485-600 °C [1]. On the other hand, the PTO thin film was heteroepitaxially grown on single crystal SrTiO_3 substrate under hydrothermal condition at 110-200 °C. In this case, powders of TiO_2 (anatase) and $\text{Pb}(\text{NO}_3)_2$, and SrTiO_3 substrate were added into various alkali hydroxide solution [2].

Previously, the BaTiO_3 thin film was prepared by the combination of hydrothermal method and electrodeposition on single crystal SrTiO_3 substrate with $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ conducting buffer layer (LSMO/STO). Namely, in the hydrothermal electrodeposition, the LSMO/STO substrate was suspended in the $\text{Ba}(\text{OH})_2$ solution including TiO_2 powder at 60-90 °C and the voltage of -1 V against Pt counter electrode was applied during the deposition. The very fine particles of BTO were epitaxially deposited on LSMO/STO substrate [3].

In this study, the hydrothermal electrodeposition was applied to prepare PbTiO_3 heteroepitaxial thin film at relatively low temperature. The film microstructure was

characterized by X-ray diffractometry (XRD) and scanning electron microscopy (SEM). The effects of preparation conditions (temperature and deposition time) were investigated.

2. EXPERIMENTAL

$\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ layer was deposited by spin-coating of precursor acetate solution on (100) oriented SrTiO_3 substrate ($5 \times 5 \times 0.5$ mm, MTI corp., California, U.S.A.) as a conductive buffer layer. The preparation of precursor acetate solution and the LSMO layer on STO substrate were described elsewhere [3, 4].

For the preparation of PTO thin film, we used an airtight NALGEN vessel (total volume: 40 ml) equipped with two clips as a reaction cell. The vessel contained 13 ml of 4M KOH solution and the mixture of 1.5 g $\text{Pb}(\text{OH})_2$ and 0.4 g TiO_2 (anatase) at the bottom. The LSMO/STO and Pt plate were suspended in the solution with metal clips as working and counter electrodes, respectively. After sealing the vessel, the temperature was kept at 90-110 °C and the voltage of 1 V (direct current) was applied between LSMO/STO and Pt electrodes (LSMO/STO was negative) during the reaction period. The schematic drawing of reaction cell is shown in Fig. 1.

The PTO film obtained was characterized by means of XRD (Rigaku RINT2200, $\text{CuK}\alpha$ radiation) and FE-SEM (Hitachi S-4200).

3. RESULTS AND DISCUSSION

Figure 2 shows the x-ray diffraction pattern of PTO

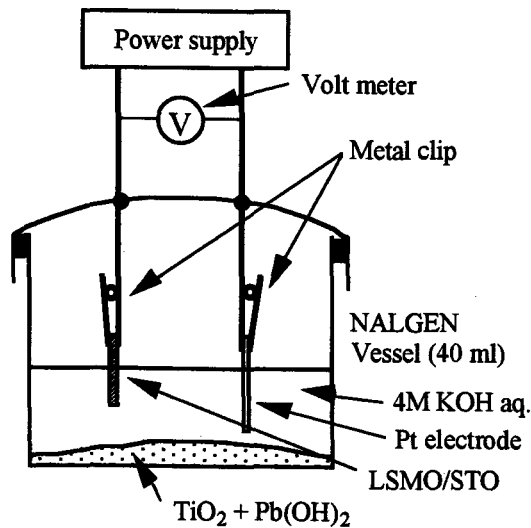


Fig. 1 Schematic drawing of reaction cell.

film grown by hydrothermal electrodeposition at 90 °C for 24 h. The patterns in the 2θ range from 40 to 45° are magnified at the corner for the films grown at 90–110 °C. The diffraction peak observed around 43° was assigned to PTO (002). No other peak except for STO (200) and LSMO (200) appeared in the range of 30–60°. This means that the PTO film is oriented along with c-axis perpendicular to LSMO/STO substrate. The lattice constant of a-axis for tetragonal PTO unit cell (0.3896 nm) is almost the same as that of a-axis for cubic STO unit cell (0.3904 nm), inducing the c-axis orientation of

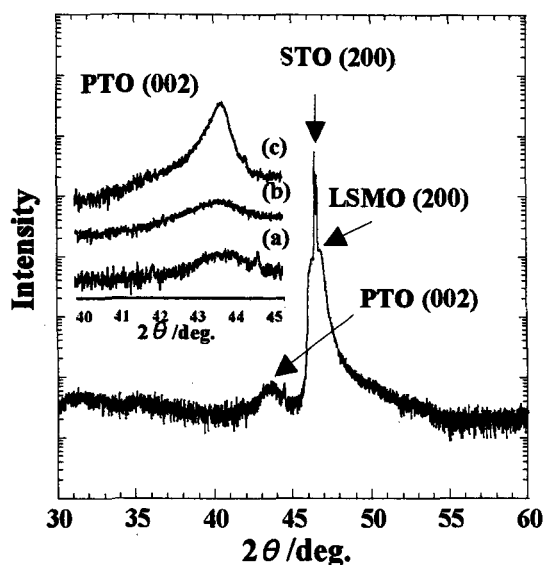


Fig. 2 X-ray diffraction pattern of PTO film grown by hydrothermal electrodeposition at 90°C for 24 h. The magnified patterns for PTO (002) are shown for the films grown at (a) 90 °C, (b) 100 °C and (c) 110 °C

PTO film. The LSMO was reported to have pseudo-cubic structure with slightly smaller lattice constant than STO [5]. Thus, it is assumed that LSMO buffer layer hardly affects the orientation of PTO film. The height of PTO (002) peak increased with increasing deposition temperature, suggesting that the thickness of film and thus the rate of film growth were enhanced at higher temperature.

Figure 3 shows the surface SEM images of PTO film at the center part of substrate grown by hydrothermal electrodeposition at 90–110 °C for 24 h. From the all images, it is seen that the PTO film completely covered the substrate. In the hydrothermal deposition of PTO film [2], the deposition temperature of 150 °C was necessary for obtaining the fully covered PTO film. It is noteworthy that this is attained even at 90 °C for the hydrothermal electrodeposition method in this study. For the PTO film grown at 90 °C (Fig. 3-a), the large rectangular shaped crystallites (200–400 nm) were observed with the same orientation. This suggests that the rectangular shape of crystallite reflects the shape of (100) face of PTO unit cell and that the film is epitaxially grown on the substrate with the same orientation. The surface was almost flat although the difference of step height between crystallites was visible. When the film was grown at 100 °C (Fig. 3-b), the film consisted of the rectangular crystallite of moderate size (below 100 nm) and very fine particles. For the film grown at 110 °C (Fig. 3-c), the large rectangular crystallite was not observed and the aggregation of fine particles (~20 nm) was observed at the edge of crystal plane. It was found that the growth mode was quite different between growth temperatures. The rate of film growth is small at 90 °C, suggesting that the film has enough time to prepare large ordered crystal. At higher temperature, the deposition of fine particle is promoted, inducing the disappearance of large ordered crystallite. However, it is assumed from XRD results that such fine particles are also oriented with c-axis direction.

From FWHM of the PTO (002) peak, the crystallite size of PTO (002) was calculated according to Scherrer's formula. The results are shown in Fig. 4 as a function of growth temperature. The crystallite size was as small as 8 nm at 90 °C and increased to 21 nm with increasing growth temperature. In Fig. 3-a, such fine crystallites were not observed. Because $\langle 002 \rangle$ is the direction perpendicular to the substrate, it is assumed that the crystallite size of PTO (002) reveals the average thickness of PTO film.

In order to explain the initial growth stage, the SEM images of PTO film grown at 90 °C for 10 h are shown in

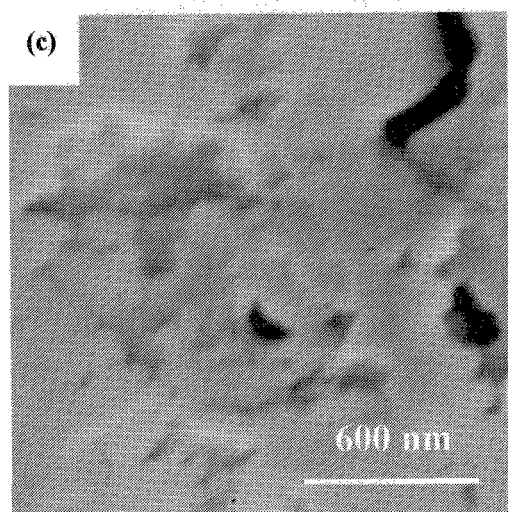
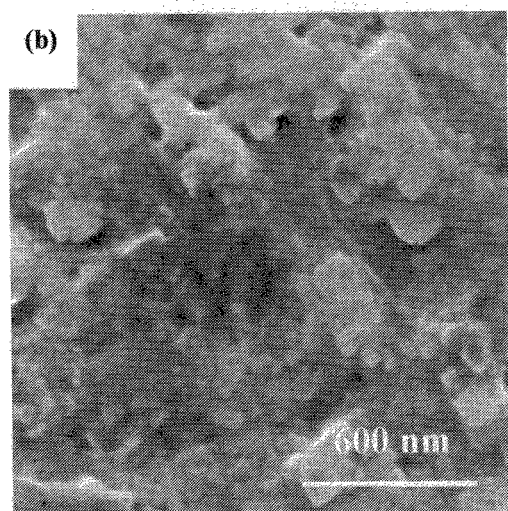
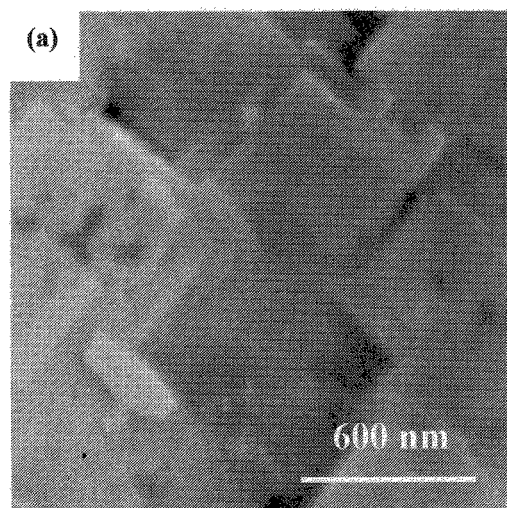


Fig. 3 Surface SEM images of PTO film at the center of substrate grown by hydrothermal electrodeposition for 24 h at (a) 90 °C, (b) 100 °C and (c) 110 °C.

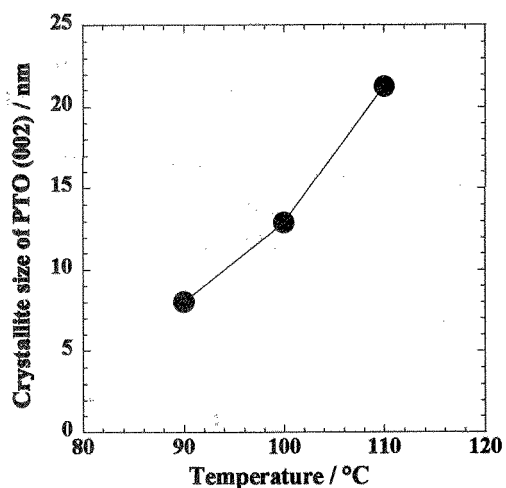


Fig.4 Crystallite size of PTO (002) calculated from Scherrer's formula as a function of growth temperature.

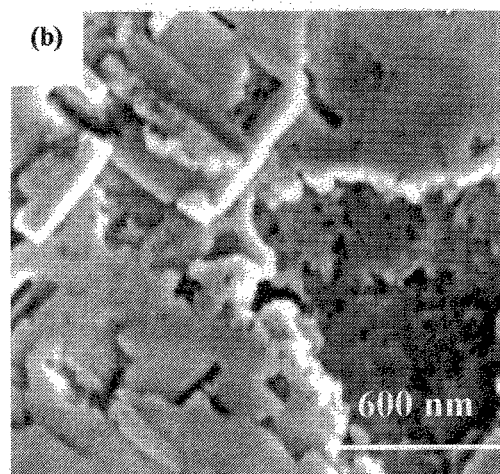
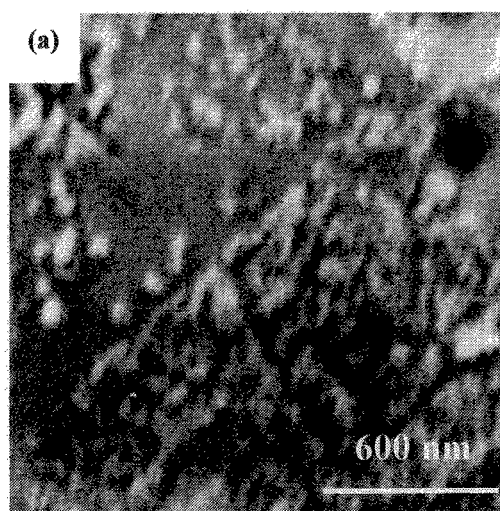


Fig.5 Surface SEM images of PTO film grown at 90 °C for 10 h. (a) Upper part, and (b) bottom part of substrate.

Fig. 5. Fig. 5-a is the image at the upper part of substrate, while Fig. 5-b is at the bottom part. The PTO film did not completely cover the whole LSMO/STO substrate after 10 h deposition. The surface morphology changed from upper part to bottom of substrate, suggesting that the growth mechanism could be observed for the film grown with short period. From Fig. 5-a, it was seen that fine and cubic particles of PTO (~20 nm) were deposited and underlying LSMO layer was visible. The LSMO film had a few pinholes and the wave undulation. When the film grew further (Fig. 5-b), the large crystallite having flat surface appeared although the edge of crystallite was disordered. It is noted that the microstructure of aggregation of fine particles is observed under the large crystallite. These results suggest that the film growth progresses with the aggregation of fine particle of PTO with the same orientation. First, the PTO fine particles are deposited on LSMO and fill the undulation of LSMO. Then the fine particles are united to form large crystallite and attracted to large crystallite for further growth of crystallite, as demonstrated by Zukoski *et al.* [6, 7]. The flat surface of crystallite means that the rate of growth is larger in <100> direction than <001> direction.

Previously, the BTO film was epitaxially grown on LSMO/STO substrate by hydrothermal electrodeposition [3]. The colloidal nuclei of BTO were formed near TiO₂ powder. Then, such nuclei were attracted electrophoretically to negatively charged LSMO/STO electrode and deposited epitaxially. Thus, the BTO film consisted of fine particle and completely covered the substrate. In this study, the similar phenomenon is considered to occur in the PTO film growth. The source of fine particle of PTO is assumed to be PTO colloidal nuclei formed by the reaction of TiO₂ with Pb(OH)₂. In the case of PTO deposition, the fine particles are deposited on the substrate and united to form large crystallite. Since the powders of TiO₂ and Pb(OH)₂ are precipitated at the bottom of NALGEN vessel, the concentration of nuclei is high near the powder and decreases toward the upper part of vessel. It is considered that the change in morphology between the upper part and the bottom of LSMO/STO substrate (Fig. 5) results from the variation of nuclei concentration in the vessel.

4. CONCLUSIONS

The PTO thin film was epitaxially grown on single crystal STO substrate with LSMO conductive buffer layer by hydrothermal electrodeposition method. The colloidal nuclei of PTO formed by the reaction of TiO₂

with Pb(OH)₂ in alkali solution were attracted electrophoretically to LSMO/STO substrate and deposited with the same orientation. The film consisted of fine and cubic particle of ~20 nm at initial stage of film growth. Then the fine particles were united to form large crystallite and attracted to large crystallite for further growth. The PTO film with almost flat surface was obtained after 24 h deposition at 90 °C.

ACKNOWLEDGMENT

Authors express great thanks to the Industrial Research Center of Shiga Prefecture for the measurement of SEM.

REFERENCES

- [1] M. C. Gelabert, R. A. Laudise, R. E. Riman, *J. Crystal Growth*, **197**, 195-203 (1999).
- [2] A. T. Chien, J. Sacleben, J. Speck, and F. F. Lange, *J. Mater. Res.*, **14**, 3303-3311 (1999).
- [3] J. Tamaki, G. K. L. Goh, and F. F. Lange, *J. Mater. Res.*, **15**, 2583-2586 (2000).
- [4] A. D. Polli, F. F. Lange, M. Ahlskog, R. Menon, and A. K. Cheetham, *J. Mater. Res.*, **14**, 1337-1342 (1999).
- [5] T. Manabe, I. Yamaguchi, W. Kondo, S. Mizuta, and T. Kumagai, *J. Mater. Res.*, **12**, 541-545 (1999).
- [6] S. Kim and C. F. Zukoski, *J. Colloid and Interface Sci.*, **139**, 198-212 (1990).
- [7] G. H. Bogush and C. F. Zukoski, *J. Colloid and Interface Sci.*, **142**, 19-34 (1991).

(Received December 20, 2001; Accepted January 31, 2002)