Transactions of the Materials Research Society of Japan 28 [4] 1215-1218 (2003)

Synthesis of Barium Strontium Titanate Thin Film by Hydrothermal Electrodeposition

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$Ba_{1-x}Sr_xTiO_3$ (BST) thin films have been synthesized on $LaAlO_3$ single crystal substrate equipped with $La_{0.7}Ca_{0.3}MnO_3$ conducting buffer layer (LCMO/LAO) by means of hydrothermal electrodeposition method at 80 °C. The $Ba(OH)_2$-$Sr(OH)_2$ mixed solution was used for the preparation of BST films. The BST grains of cubic crystal structure with 7-40 nm in size were deposited on the LCMO/LAO substrate with (200) orientation. Further, the (200) peak position shifted to higher degree side in XRD with increasing Sr^{2+} concentration in mixed solution. This indicates that the composition of film can be varied with the composition of $Ba(OH)_2$-$Sr(OH)_2$ mixed solution. The Sr content in film was largely higher than that in solution, suggesting that Sr^{2+} was easily taken in the perovskite structure compared with Ba^{2+} in BST system. On the other hand, the composition of film strongly influenced the film microstructure. The grain size was ca. 40 nm for $BaTiO_3$ film, while the size was decreased with increasing Sr content in the film. The feature of this method is that the oxide film with fine grains can be prepared at low temperature.
Key words: Barium strontium titanate, Epitaxial growth, Hydrothermal electrodeposition

1. INTRODUCTION

Perovskite-type oxides such as $BaTiO_3$ (BTO), $Ba_{1-x}Sr_xTiO_3$ (BST), $PbTiO_3$ (PTO) and $PbZr_{1-x}Ti_xO_3$ (PZT) are well known as typical ferroelectric materials and have been used for capacitors, nonvolatile memories, and pyroelectric sensors in electronic industry. These days, soft-solution process, in which an oxide thin film is directly synthesized from solution under mild condition, is increasingly attractive as low energy consumption process [1]. Concerning above perovskite-type oxides, the mild hydrothermal method (90-150 °C) was employed for the epitaxial growth of BTO, PTO, and PZT films on $SrTiO_3$ or $LaAlO_3$ single crystal substrate [2-5]. Further, we have recently proposed the hydrothermal electrodeposition method for the preparation of such oxide films at lower temperatures, i.e., BTO film was prepared at 60-90 °C [6] and PTO film was at 90-110 °C [7]. Moreover, it was found that the unique feature of hydrothermal electrodeposition was the deposition of very fine grains of a few tens nm.

In this paper, we tried to prepare BST thin film on $LaAlO_3$ single crystal substrate (LAO) by means of hydrothermal electrodeposition at 80 °C. The effect of solution composition on film composition and film microstructure was evaluated.

2. EXPERIMENTAL

$La_{0.7}Ca_{0.3}MnO_3$ layer (LCMO) was deposited by spin-coating of precursor acetate solution on (100) oriented $LaAlO_3$ substrate ($5\times5\times0.5^t$ mm, Shinkosha, Japan) as a conducting buffer layer. The substrate with conducting layer was denoted as LCMO/LAO hereinafter. The precursor acetate solution for LCMO deposition was prepared from $La(OH)_3$, $CaCO_3$, and MnO as described elsewhere [8].

BST thin films with various compositions were deposited on LCMO/LAO substrate by hydrothermal electrodeposition. 1 g of TiO_2 (anatase) powder was added into 13 ml of mixed solution of $Ba(OH)_2$ and $Sr(OH)_2$ at 80 °C. LCMO/LAO substrate and Pt counter electrode were suspended in the solution, and the voltage of 1 V (direct current) was applied between electrodes (LCMO/LAO : negative, Pt : positive) for 24h. The concentration ratio of $Ba(OH)_2$ and $Sr(OH)_2$ was changed within total concentration of 0.5 M. The detail of film deposition is referred to refs. 6 and 7.

The crystal structure, film composition, and microstructure of BST film were characterized by means of XRD (Rigaku RINT2200, CuKα radiation), XPS (Perkin-Elmer ESCA5000, AlKα radiation) and FE-SEM (Hitachi S-4300). The peak position in XRD pattern was estimated by means of curve fitting software. The binding energies in XPS were referred to C1s =

285.0 eV.

3. RESULTS AND DISCUSSION

Figure 1 shows the XRD patterns of BST thin films grown on LCMO/LAO substrate in $Sr(OH)_2$-$Ba(OH)_2$ mixed solution with various compositions. The diffraction peak ascribable to BST was observed only in the range of 45-46°. Other than this peak, LAO (200) and LCMO (200) peaks were observed at 47.98 and 46.90°, respectively, in the range 30-60°. The peak for $BaTiO_3$ film prepared from $Ba(OH)_2$ solution was observed at 44.98°. If this diffraction peak is assigned to (200) peak of cubic structure, the lattice constant is estimated as 0.4026 nm. This value is good agreement with that for cubic $BaTiO_3$. Thus, the results indicate the (200) orientation of $BaTiO_3$ film grown on LCMO/LAO single crystal substrate. On the other hand, the $SrTiO_3$ (200) peak could not be observed because the thickness was too thin. The thick $SrTiO_3$ film was grown at 80 °C for 48h by hydrothermal method. The $SrTiO_3$ (200) peak was observed for the thick $SrTiO_3$ film and the lattice constant was estimated as 0.3909 nm. The lattice constants of both end-members of $BaTiO_3$ (0.4026 nm) and $SrTiO_3$ (0.3909 nm) films were considered to be very similar to lattice constant for cubic $BaTiO_3$ and cubic $SrTiO_3$ in JCPDS data [9].

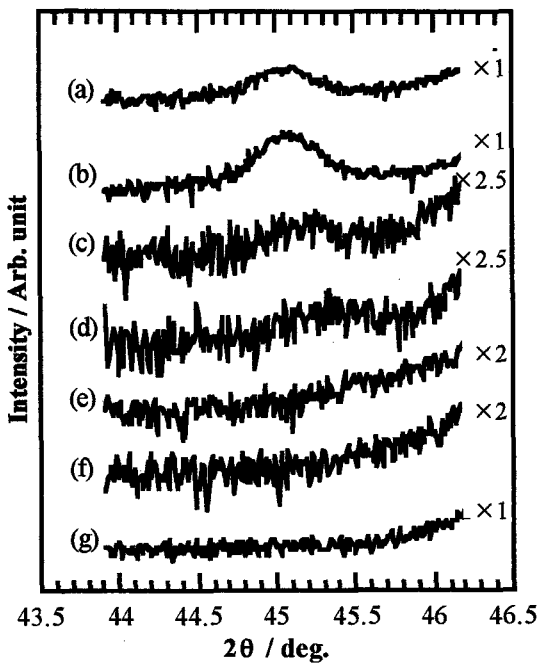

Fig. 1 X-ray diffraction patterns of BST films prepared from various $Ba(OH)_2$-$Sr(OH)_2$ mixed solution by hydrothermal electrodeposition.
Sr^{2+} concentration : (a) 0 M, (b) 0.01 M, (c) 0.025 M, (d) 0.05 M, (e) 0.1 M, (f) 0.15 M, (g) 0.20 M.

As seen in Fig. 1, the BST (200) peak shifted to higher degree side with increasing Sr^{2+} concentration in the mixed solution. This suggests the formation of BST solid solution and that Sr content in solid solution increases with increasing Sr^{2+} concentration. The (200) peak became obscure when Sr^{2+} concentration was higher than 0.1 M because the peak became broader and overlapped with large LCMO (200) peak. The lattice constants of BST films were calculated from position of (200) peak in the Sr^{2+} concentration range of 0-0.05 M, and summarized in Fig. 2 as a function of Sr^{2+} concentration in the mixed solution. In the structural study of $BaTiO_3$-$SrTiO_3$ system [10], the lattice constant of a-axis almost linearly changed from $BaTiO_3$ to $SrTiO_3$ with increasing Sr content in the system. According to this report, the bulk composition of BST could be estimated from lattice constant in Fig. 2. For example, the bulk composition of BST film obtained from 0.45 M $Ba(OH)_2$-0.05 M $Sr(OH)_2$ mixed solution was estimated as $Ba_{0.75}Sr_{0.25}TiO_3$ from the guide of broken arrow. The Sr content in BST film was larger than respective Sr content in mixed solution, suggesting that Sr^{2+} was easily taken in the perovskite structure compared with Ba^{2+} in BST system. This relation had good agreement with the report by Kajiyoshi et al [11], in which BST thin films were prepared by anodic oxidation of Ti electrode in $Ba(OH)_2$-$Sr(OH)_2$ mixed

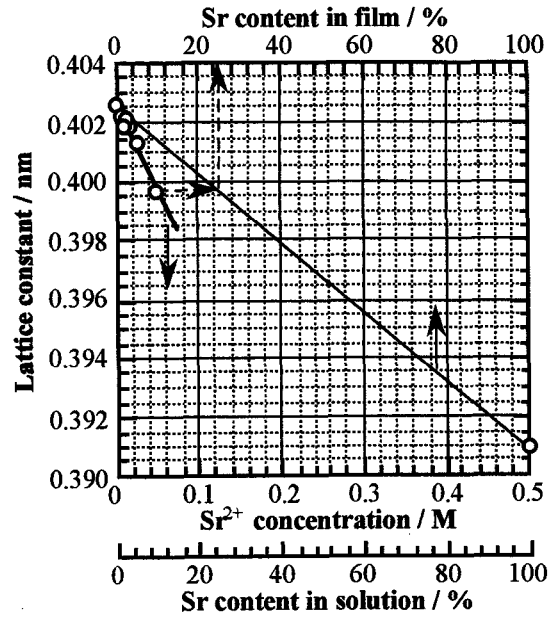

Fig. 2 Lattice constants BST films prepared by hydrothermal electrodeposition as a function of Sr^{2+} concentration in mixed solution. Estimated Sr content in film is also shown.

solution at 150 °C.

From the XRD results, the lattice mismatch was evaluated as follows. $LaAlO_3$ has cubic structure with lattice constant of 0.3788 nm, while $La_{0.7}Ca_{0.3}MnO_3$ is pseudo-cubic with lattice constant of 0.387 nm [8]. Thus, the lattice mismatch of LCMO from LAO is estimated as +2.2%. The mismatch of $BaTiO_3$ from LCMO is +4.0%, while that of $SrTiO_3$ from LCMO is +1.0%. The mismatch of BST from LCMO is considered to be between both end-members. As demonstrated for $BaTiO_3$ thin film grown on $La_{0.7}Sr_{0.3}MnO_3/SrTiO_3$ single crystal substrate by hydrothermal electrodeposition [6], the BST films in this paper is considered to also epitaxially grow on LCMO/LAO substrate.

The surface compositions of BST films prepared by hydrothermal electrodeposition were estimated from the ratio of peak areas in Ba3d and Sr3d levels in XPS. The surface Sr content in the film is shown in Fig. 3 as a function of Sr^{2+} concentration in mixed solution. The bulk Sr content estimated from Fig. 2 is also plotted in the figure. It was found that the surface composition was the same as the bulk composition for the film prepared from $Ba(OH)_2$-$Sr(OH)_2$ mixed solution with Sr^{2+} concentration less than 0.05 M. However, Ba existed at the surface of film prepared from the solution with high Sr^{2+} concentration (0.15-0.25 M). In the BST film prepared by anodic oxidation of Ti in 50:50 $Ba(OH)_2$-$Sr(OH)_2$ mixed solution (corresponding to

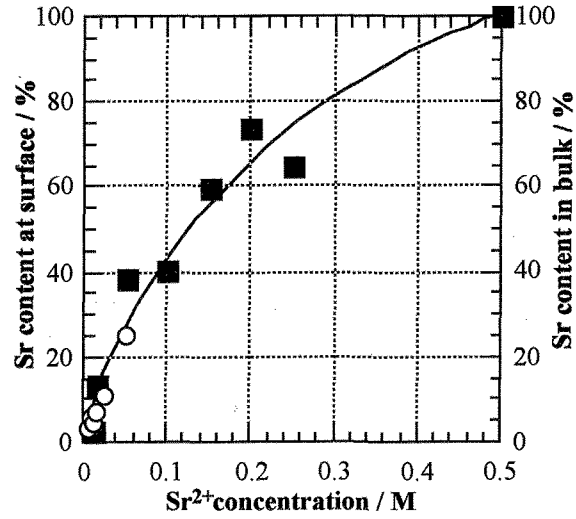

Fig. 3 Surface Sr content (■) of BST films as a function of Sr^{2+} concentration in mixed solution. Bulk Sr content (○) estimated from Fig. 2 is also shown.

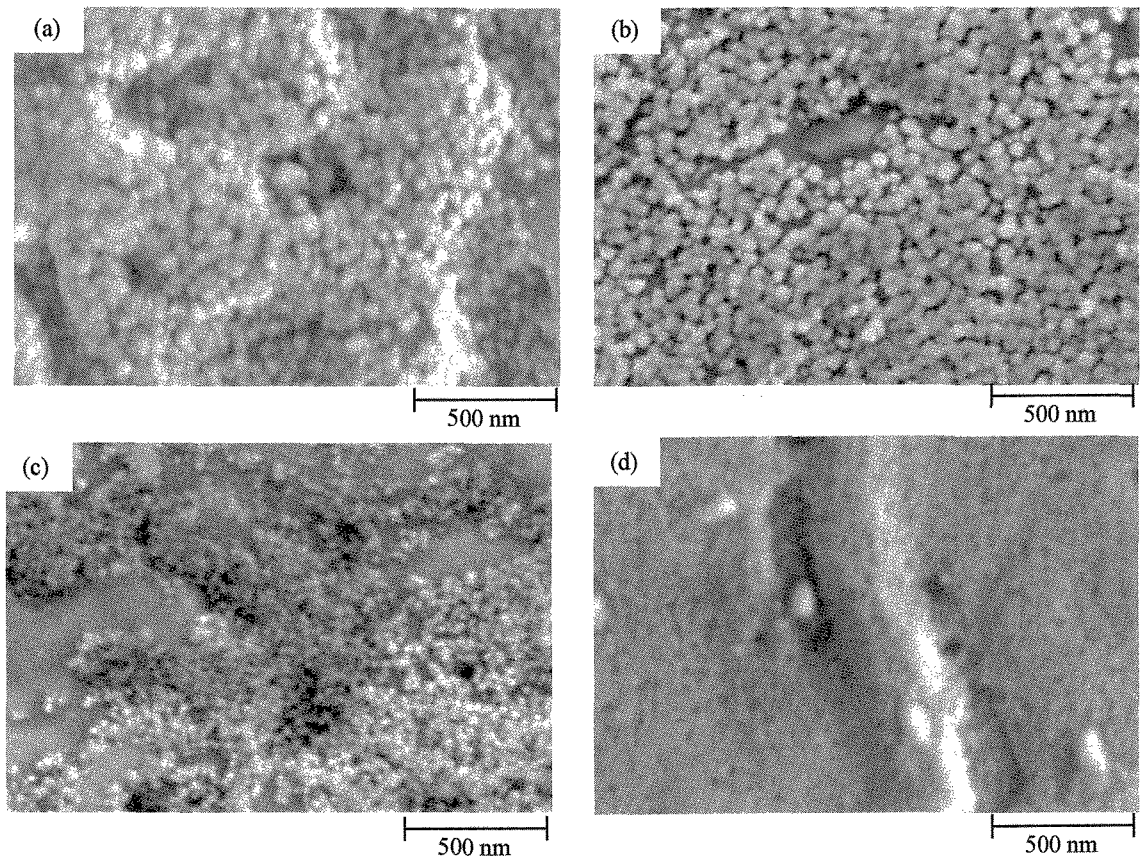

Fig. 4 Surface SEM images of BST films prepared from various $Ba(OH)_2$-$Sr(OH)_2$ mixed solution by hydrothermal electrodeposition. Sr^{2+} concentration : (a) 0 M, (b) 0.1 M, (c) 0.2 M, (d) 0.5 M.

0.25 M Sr^{2+} in this paper) [10], Ba is hardly incorporated into perovskite structure ($Ba_{0.04}Sr_{0.96}TiO_3$ is obtained). The surface might be Ba-rich for the BST film prepared in high Sr^{2+} concentration.

Fig. 4 shows the surface SEM images of BST thin films with various Sr compositions prepared by hydrothermal electrodeposition. It is seen from Fig. 4 (a)-(c) that the film consists of oriented arrangement of almost square shaped grains. It is considered that the shape of grain originates from cubic structure of perovskite unit cell and that the oriented arrangement indicates the epitaxial growth of BST on LCMO/LAO single crystal substrate. Further, it was clearly observed that the grain size of BST was decreased with increasing Sr content in the film. The average grain size of BST is plotted in Fig. 5 as a function of Sr concentration in mixed solution. The average grain size of $BaTiO_3$ was as large as 40 nm. The size was decreased to 7 nm for $SrTiO_3$ with increasing Sr concentration. The decrease in grain size with increasing Sr concentration was well consistent with the broadening of (200) peak in XRD patterns (Fig. 1). As indicated previously [6, 7], it was again demonstrated that the feature of hydrothermal electrodeposition was the deposition of fine grains. Further, it was found that the BST grain with large Ba content easily grew to large one, while Sr suppressed the grain growth in BST with large Sr content or $SrTiO_3$. In the hydrothermal electrodeposition, the following mechanism has been proposed [6]. Namely, the colloidal particles formed in the solution were electrophoretically attracted to the electrode and deposited epitaxially on single crystal electrode. It is assumed that the composition of BST affects the growth of colloidal particles due to collision in the solution.

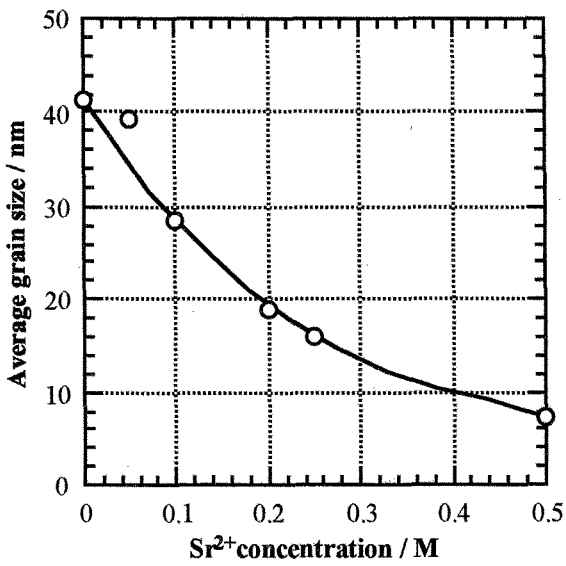

Fig. 5 Average grain sizes of BST prepared by hydrothermal electrodeposition as a function of Sr^{2+} concentration in mixed solution.

4. CONCLUSIONS

$Ba_{1-x}Sr_xTiO_3$ thin films were epitaxially grown on $LaAlO_3$ single crystal substrate with $La_{0.7}Ca_{0.3}MnO_3$ conducting buffer layer by means of hydrothermal electrodeposition. The film composition was controlled by changing the solution composition in $Ba(OH)_2$-$Sr(OH)_2$ mixed solution. It was found that Sr^{2+} was easily taken in perovskite structure and that the grain size decreased with increasing Sr content in the film. The feature of this method was the deposition of fine grains.

ACKNOWLEDGMENT

Authors express great thanks to Prof. H. Namba of Department of physical Sciences at Ritsumeikan University for the measurement and discussion on XPS.

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(Received December 20, 2002; Accepted January 31, 2003)