

Annealing conditions for preparation of epitaxial BaTiO₃ thin films on SrTiO₃ by dipping-pyrolysis process

S. Kim*, T. Manabe, I. Yamaguchi, T. Kumagai and S. Mizuta

*National Institute of Materials and Chemical Research
Higashi 1-1, Tsukuba, Ibaraki 305, Japan*

Epitaxial BaTiO₃ thin films were prepared on SrTiO₃ (100) substrates by dipping-pyrolysis process using a mixed solution of barium and titanium naphthenates, and effects of annealing conditions, i.e., temperature and atmosphere, on crystallization of BaTiO₃ films were investigated. Crystallinity of BaTiO₃ thin films depends not only on final heat-treatment conditions but on pyrolysis conditions; highly oriented BaTiO₃ thin films were obtained by prefiring between 440° and 550°C, followed by final heat treatments at 750°C and above. In addition, crystallization of BaTiO₃ was found to proceed at lower temperatures under atmospheres with lower oxygen partial pressures ($p(O_2)$). Epitaxy of these films was confirmed by x-ray pole-figure analysis.

1. INTRODUCTION

Ferroelectric BaTiO₃ films are of much interest for electronic device applications, and epitaxial BaTiO₃ thin films having a smooth surface are required for electro-optical applications to achieve lower propagation loss. Currently, lots of attempts have been done to prepare the epitaxial BaTiO₃ thin films by various film deposition processes such as metalorganic chemical vapor deposition (MOCVD) [1-3], activated reactive evaporation [4], radio-frequency sputtering [5,6] and pulsed laser deposition [7,8], on a variety of substrates, e.g., MgO [1,5], LaAlO₃ [2,3] and SrTiO₃ [6].

Among various thin film fabrication processes, dipping-pyrolysis (DP) process or metalorganic deposition (MOD) has the following advantages: it is a simple and low-cost chemical process and is easily applicable to films with any shape and size. Recently, the authors have succeeded in fabricating epitaxial BaTiO₃ thin films by this process [9]. In this paper, BaTiO₃ thin films were prepared on SrTiO₃ (100) by DP process varying the firing conditions, i.e., temperature and oxygen-partial pressure ($p(O_2)$), for pyrolysis and final heat treatment, and the effects of these parameters on the

crystallization of BaTiO₃ films were investigated.

2. EXPERIMENTAL

The coating solution was prepared by mixing barium naphthenate and titanium naphthenate with a molar ratio of Ba/Ti = 1.0 and by diluting it with toluene to decrease the viscosity. This solution was spin-coated (2000 rpm, 5 s) onto SrTiO₃ (100) substrates, of which the lattice-misfit values with tetragonal BaTiO₃ are 2.3% and 3.4% along *a*-axis and *c*-axis, respectively. The coated films were pre-fired at temperatures between 400° and 550°C for 10 min in air by rapid thermal annealing to pyrolyze metal naphthenates and to eliminate organic components. The spin-coating and pyrolysis were repeated to adjust the thickness of the precursor films to be about 0.7 μm. The precursor films were further heat-treated at various temperatures between 700° and 850°C for 1 h in air or in a low- $p(O_2)$ atmosphere in a tube furnace. The low- $p(O_2)$ environment was set by flowing a gas mixture of Ar and O₂; the $p(O_2)$ at the outlet of the tube furnace was measured to be 2×10^{-4} atm by zirconia oxygen analyzer. Alignment of films was

* On leave from Department of Chemical Engineering, Yosu Fisheries University, Yosu 550-749, Korea

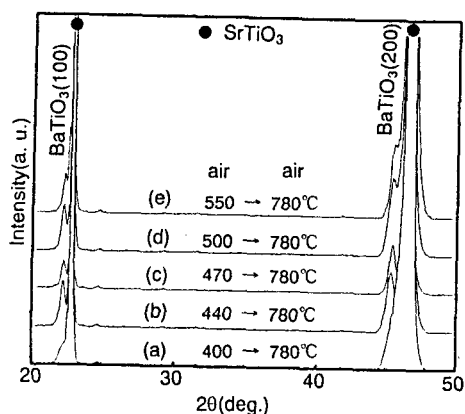


Figure 1. XRD θ - 2θ scans of the BaTiO₃ films pyrolyzed at 400°C (a), 440°C (b), 470°C (c), 500°C (d) and 550°C (e) and then heat-treated at 780°C in air.

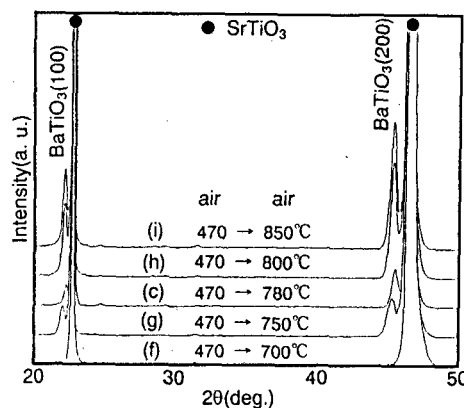


Figure 2. XRD θ - 2θ scans of the BaTiO₃ films pyrolyzed at 470°C and then heat-treated at 700°C (f), 750°C (g), 780°C (c), 800°C (h) and 850°C (i) in air.

examined by x-ray diffraction (XRD) θ - 2θ scans and pole figures using Cu K_{α} radiation. The surface morphology of thin films was observed by scanning electron microscopy (SEM).

3. RESULTS AND DISCUSSION

First, the effect of pyrolysis temperature was investigated; the coated films were pyrolyzed at temperatures ranging from 400° to 550°C while the final heat-treatment temperature was fixed at 780°C. Both heat treatments were carried out in air. XRD θ - 2θ scans for the films pyrolyzed at 400° - 550°C showed that these pre-fired films were all amorphous and the difference among them was not significant. However, after final heat-treatment at 780°C, remarkable difference was recognized in the crystallinity of final BaTiO₃ films. Figure 1 shows the XRD θ - 2θ scans of BaTiO₃ films (a), (b), (c), (d) and (e), after pyrolysis at 400°, 440°, 470°, 500° and 550°C, respectively, and subsequent heat treatment at 780°C. Film (a), pre-fired at 400°C, was almost amorphous and traces of BaTiO₃ (*h*00) and/or (00*l*) peaks were observed at the shoulder of peaks of SrTiO₃ substrate. By contrast, in films (b)-(e), pyrolyzed at 440° - 550°C, distinct (*h*00)/(00*l*) peaks of BaTiO₃ were recognized while other peaks of BaTiO₃ were faint, showing that the BaTiO₃ films

were preferentially oriented with [100]- and/or [001]-axis perpendicular to the substrate surface. These results indicate that highly oriented BaTiO₃ films could be obtained by pyrolysis at temperature ranges from 440° to 550°C.

It is quite interesting that the crystallinity of BaTiO₃ films was significantly affected by pyrolysis (prefiring) temperature, although all the pre-fired films were amorphous by XRD θ - 2θ scans and the final heat-treatment temperature was the same. The poor crystallinity of film (a) may be attributed to the presence of undecomposed Ba-naphthenate. The results of thermogravimetry-differential thermal analysis (TG-DTA) of starting solution indicated that decomposition of Ti-naphthenate completes below 400°C, whereas that of Ba-naphthenate at around 450°C. Thus, the film pyrolyzed at 400°C is assumed to consist of amorphous or submicron-sized crystallites of TiO₂ and incomplete decomposition residue of Ba-naphthenate. In this case, it is no wonder that the segregation of TiO₂ and Ba-residue in microscale would occur, resulting in the poor crystallinity of BaTiO₃ films even after final heat treatment.

Secondly, when the pyrolysis temperature was fixed at 470°C, the temperatures for final heat treatment were varied between 700° and 850°C in air. Figure 2 shows XRD θ - 2θ scans for the final BaTiO₃ films (f), (g), (h) and (i), heat-treated at

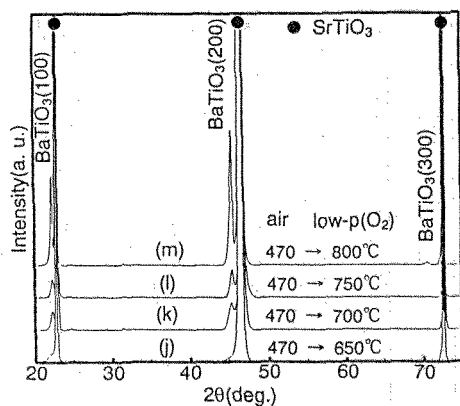


Figure 3. XRD θ - 2θ scans of the BaTiO₃ films pyrolyzed at 470°C, and then heat-treated at 650°C (j), 700°C (k), 750°C (l) and 800°C (m) under low $p(\text{O}_2)$ of 2×10^{-4} atm.

700°, 750°, 800° and 850°C, respectively; this figure also includes the data of film (c), annealed at 780°C, in Fig. 1. In film (f), heat-treated at 700°C, the peaks of BaTiO₃ were hardly seen. In films (g)-(i) and (c), heat-treated at 750°C and above, the (h00)/(00l) peaks of BaTiO₃ alone were observed; the higher the heat-treatment temperature the stronger the BaTiO₃ peaks. Using the substrate SrTiO₃ (200) peak as an internal calibration standard, the lattice parameter of epitaxial BaTiO₃ film (i), heat-treated at 850°C, along the direction perpendicular to the substrate surface was determined to be 0.399₉ nm. This value is close to the *a*-axis lattice parameter ($a_0 = 0.3994$ nm) rather than *c*-axis one ($c_0 = 0.4038$ nm) of tetragonal BaTiO₃, and is similar to those of the BaTiO₃ films prepared on MgO[1] and on LaAlO₃[3] by MOCVD. The lattice parameter of film (i) along the direction parallel to the substrate surface will be reported elsewhere [9].

Thirdly, the precursor films, pyrolyzed at 470°C in air, were also heat-treated under a low- $p(\text{O}_2)$ atmosphere of 2×10^{-4} atm. Figure 3 shows the XRD θ - 2θ scans of films (j), (k), (l) and (m), heat-treated at 650°, 700°, 750° and 800°C, respectively. In film (j), heat-treated at 650°C, only traces of BaTiO₃ peaks were observed at the shoulder of SrTiO₃ peaks. On the other hand, in films (k)-(m), heat-treated at 700°C and higher, strong BaTiO₃ (h00)/(00l) peaks

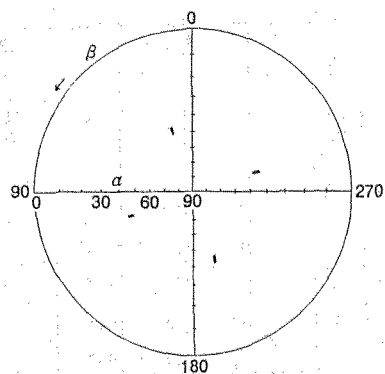


Figure 4. Pole figure of BaTiO₃ (110)/(101) reflection for film (l).

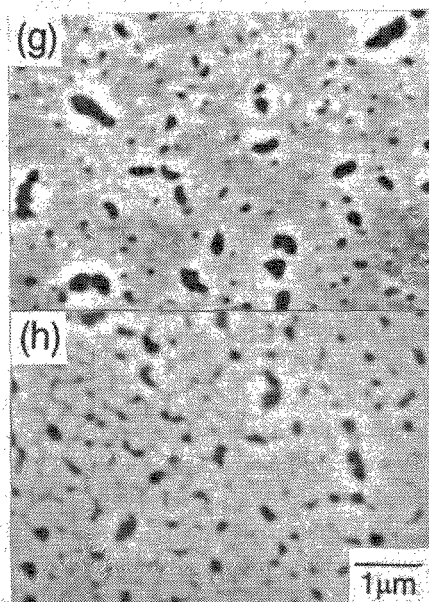


Figure 5. Surface morphologies of the films heat-treated at 750°C (g) and 800°C (h) in air.

were observed. Comparison of Fig. 3 with Fig. 2 revealed that the intensities of the peaks in Fig. 3 are stronger than those in Fig. 2 when the heat-treatment temperature was the same; for example, film (m), annealed under low- $p(\text{O}_2)$ atmosphere exhibited stronger BaTiO₃ peaks than films (h), annealed in air at the same temperature of 800°C.

Crystallization and alignment behavior of superconducting YBa₂Cu₃O_{7-y} films greatly depends on $p(\text{O}_2)$ of heat treatment, as described in our

previous papers [10, 11]. In case of $\text{YBa}_2\text{Cu}_3\text{O}_{7-y}$, such effects may be attributed to the large oxygen nonstoichiometry and the resulting changes in lattice-parameters. However, oxygen nonstoichiometry in BaTiO_3 is too small to interpret the above striking result; and therefore further experiments and analysis are required.

Further, the in-plane alignment of these films was investigated by x-ray pole-figure analysis. Films (g)-(i) and (k)-(m), that exhibit strong [100]/[001]-orientation in Figs. 2 and 3, gave similar pole patterns. A typical pole figure of BaTiO_3 (110)/(101) reflection is shown in Fig. 4. Sharp spots corresponding to [100]- and/or [001]-orientation were observed at every 90° of β angles and the positions of these β angles were agree with those for SrTiO_3 (110) reflections. This means that the BaTiO_3 thin films have an epitaxial relationship with the SrTiO_3 substrates.

Finally, Fig. 5 shows SEM photographs of free surfaces of films (g) and (h), heat-treated in air at 750° and 800°C , respectively. Although both films exhibited similar XRD patterns as shown in Figs. 2(g) and 2(h), their surface morphology was slightly different. Film (g) heat-treated at 750°C consisted of fine grains and the surface was relatively smooth in spite of the presence of some pores. Such pores were also recognized in the surfaces of the precursor films pyrolyzed at 470°C , thus, the pores are considered to form during pyrolysis of metal naphthenates. On the other hand, grain growth of BaTiO_3 was observed in film (h), heat-treated at 800°C , which consisted of round-shaped grains with a diameter about $0.3\ \mu\text{m}$. These surface morphologies of films (g) and (h) were similar to typical polycrystalline films prepared by metal-organic deposition [12], although films (g) and (h) obviously exhibited epitaxial growth of BaTiO_3 on SrTiO_3 substrates. Further work is in progress to improve the epitaxy and surface morphology of BaTiO_3 films, by optimizing pyrolysis and final heat-treatment conditions.

4. CONCLUSIONS

Epitaxial BaTiO_3 thin films were prepared on SrTiO_3 (100) substrates by dipping-pyrolysis process

using a mixed solution of barium and titanium naphthenates. Crystallinity of BaTiO_3 thin films depends not only on final heat-treatment conditions but on pyrolysis conditions, and highly oriented BaTiO_3 thin films were obtained by pre-firing between 440° and 550°C , followed by final heat treatments at 750°C and above in air, or at 700°C and higher under low- $p(\text{O}_2)$ environment of 2×10^{-4} atm. Pole-figure analysis indicated that BaTiO_3 thin films have an epitaxial relationship with the SrTiO_3 substrates.

REFERENCES

1. D. L. Kaiser, M. D. Vaudin, L. D. Lotter, Z. L. Wang, J. P. Cline, C. S. Hwang, R. B. Marinenko and J. G. Gillen, *Appl. Phys. Lett.*, 66 (1995) 2801.
2. J. Chen, L. A. Wills, B. W. Wessels, D. L. Schulz and T. J. Marks, *J. Electron. Mater.*, 22 (1993) 701.
3. L. A. Willis, B. W. Wessels, D. S. Richeson and T. J. Marks, *Appl. Phys. Lett.*, 60 (1992) 41.
4. Y. Yano, K. Iijima, Y. Daitoh, Y. Bando, Y. Watanabe, H. Kasatani and H. Terauchi, *J. Appl. Phys.*, 76 (1994) 7833.
5. S. Kim, S. Hishita, Y. M. Kang and S. Baik, *J. Appl. Phys.*, 78 (1995) 5604.
6. M. Matsuoka, K. Hoshino and K. Ono, *J. Appl. Phys.*, 76 (1994) 1768.
7. T. Nose, H-T. Kim and H. Uwe, *Jpn. J. Appl. Phys.*, 33 (1994), 5259.
8. V. Srikant, E. J. Tarsa, D. R. Clarke and J. S. Speck, *J. Appl. Phys.*, 77 (1995) 1517.
9. S. Kim, T. Manabe, I. Yamaguchi, T. Kumagai and S. Mizuta, *J. Mater. Res.*, to be submitted.
10. T. Kumagai, T. Manabe, H. Minamiue, W. Kondo and S. Mizuta, *Jpn. J. Appl. Phys.*, 29 (1992) L940.
11. T. Kumagai, H. Yamasaki, K. Endo, T. Manabe, H. Niino, T. Tsunoda, W. Kondo, S. Mizuta, *Jpn. J. Appl. Phys.*, 32 (1993) L1602.
12. W. O.-Benomar, S. S. Xue, R. A. Lessard, A. Singh, Z. L. Wu and P. K. Kuo, *J. Mater. Res.*, 9 (1994) 970.