Available online at www.sciencedirect.com
ScienceDirect
Ceramics International 34 (2008) 1223–1227
CERAMICS INTERNATIONAL
www.elsevier.com/locate/ceramint

Stoichiometry control and structure evolution in hydrothermally derived (Ba,Sr)TiO$_3$ films

Jianling Zhao [a,b,*], Xiaohui Wang [b], Longtu Li [b], Xixin Wang [a], Yangxian Li [a]

[a] School of Material Science and Engineering, Hebei University of Technology, Tianjin 300130, PR China
[b] State Key Lab of New Ceramics and Fine Processing, Department of Materials Science and Engineering, Tsinghua University, Beijing 100084, PR China

Received 19 October 2006; received in revised form 22 December 2006; accepted 1 March 2007
Available online 12 April 2007

Abstract

(Ba,Sr)TiO$_3$ films were synthesized on the titanium metal substrates in solution of Ba(OH)$_2$ and Sr(OH)$_2$ by hydrothermal method. Crystallinity and microstructure of the films changed with time, concentration and temperature. Effects of the mole ratio of barium and strontium in solution on the composition of film have been studied. The barium contents in the BST films are fairly lower than those in the original solutions. This indicates that strontium is more readily incorporated into the BST films, relative to barium. The results of narrow-scan of XPS spectrum confirm that the valences of Ba, Sr, Ti and O elements of hydrothermally prepared BST films are +2, +2, +4, and −2, respectively. SEM photographs show that the BST films are dense and well-compact. AFM analyses show that the average surface roughness of the films is 40–50 nm. It is concluded that BST films of different mole ratio of barium and strontium with thickness of up to 2 μm have been prepared successively by the environmentally benign hydrothermal method.

Keywords: Barium strontium titanate; Hydrothermal syntheses; Ceramic films

1. Introduction

The film of perovskite barium strontium titanate (Ba,Sr)-TiO$_3$ (BST) is an important material in the electronics industry due to its high dielectric constant and ferroelectric properties. It is among the most promising candidates for dynamic random access memories (DRAMs) and other integrated capacitors [1–3]. A variety of techniques including sol–gel, metal organic chemical vapor deposition (MOCVD), pulsed laser deposition sputtering and electrophoretic deposition have been used to prepare (Ba,Sr)TiO$_3$ films. Almost all these methods require high temperature to get crystalline films. Use of high temperature to deposit or heat-treat the films not only causes compatibility problems with silicon technology, but also induces thermal stress in the films. In order to overcome these problems, fabricating ceramic films at lower temperature such as hydrothermal and electrochemical methods are gaining more attention. BaTiO$_3$, SrTiO$_3$ and (Ba,Sr)TiO$_3$ films have been prepared by hydrothermal, electrochemical and so-called hydrothermal–electrochemical methods [4–6]. Electrochemical and hydrothermal–electrochemical processes have been widely studied due to its advantages of rapid speed and lower reaction temperature. Unfortunately the films are less crystallized and easy to form inhomogeneities and cracks due to breakdown under increased voltages [7–9]. Unlike electrochemical method, hydrothermal process causes fewer cracks and can be performed on any kind of substrates deposited with titanium metal. (Ba,Sr)TiO$_3$ films have been fabricated on both titanium substrates or metal-organic precursor deposited glass substrates by hydrothermal method [10,11]. The ability to produce BST films of various compositions and thickness via hydrothermal synthesis is of particular interest, but the processing parameters have not been well understood till now. Detailed researches have been done on the influential factors of hydrothermal synthesis of BST films through metal-organic precursor [10]. However, no systematic studies are

---

* Corresponding author at: School of Material Science and Engineering, Hebei University of Technology, Tianjin 300130, PR China.
Tel.: +86 22 60204694; fax: +86 22 60204681.
E-mail address: zhaojl02@mails.tsinghua.edu.cn (J. Zhao).

0272-8842/$34.00 © 2007 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2007.03.011

available on the hydrothermal formation of $(Ba,Sr)TiO_3$ films on titanium substrates. Little work has been done on control over hydrothermal solutions conditions, such as composition, pH value and temperature, etc. On the other hand, chemical considerations such as stoichiometry control and structure evolution have received less attention.

The purposes of the present work are to systematically analyze the effects of processing parameters on the stoichiometry and structure evolution of the hydrothermal derived BST films. Here are reported studies on the various conditions under which $(Ba,Sr)TiO_3$ films can be prepared. The influences of the concentration of barium and strontium ions, reaction temperature and time on $(Ba,Sr)TiO_3$ crystallinity and microstructures have been studied.

2. Experimental procedure

Hydrothermal syntheses of $(Ba,Sr)TiO_3$ films were carried out using a $0.1\,dm^3$ high-pressure autoclave. Prior to hydrothermal syntheses, titanium substrates with purity more than 99.9% and dimension of 7 mm × 14 mm × 0.5 mm were mechanically polished to a mirror finish. Experiments were performed in the mixture of $Ba(OH)_2$ and $Sr(OH)_2$ (analytical purity) solutions of different concentrations. The solutions were prepared with deionized water previously boiled for at least 30 min to eliminate dissolved CO_2. The titanium substrates were clamped in a Teflon cushion uprightly. Then the Teflon cushion was put into the bottom of Teflon beaker. $0.05\,dm^3$ mixture of Ba $(OH)_2$ and $Sr(OH)_2$ solution was poured into the beaker, which was immediately put in the high-pressure autoclave. The autoclave was sealed at once and put into oven at suitable temperature. After hydrothermal reaction the samples were taken out of the beaker, rinsed with CO_2-free deionized water for three times and dried for characterization.

The surface morphologies of the samples were investigated both by scanning electron microscopy (SEM) (JSM-6301, JEOL Inc., Japan) and by atomic force microscopy (AFM) (Picoscan, Molecular Imaging, USA). X-ray diffraction measurements were performed on D/max-RB diffractometer (Rigaku, Rotafles). X-ray photoelectron spectroscopy (XPS) analysis was conducted on AEM PHI5300 spectrometer using Al Kα (1468.6 eV) radiation.

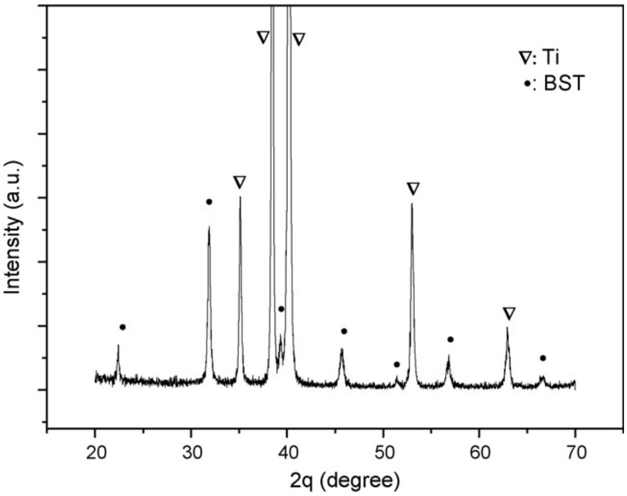

Fig. 1. X-ray pattern of BST films prepared by hydrothermal method.

3. Results and discussion

3.1. Effects of reaction conditions on the crystallinity of BST film

The typical X-ray diffraction pattern of BST films obtained by hydrothermal method is given in Fig. 1. The diffraction pattern shows the presence of crystalline cubic BST without any preferred orientation.

The crystallinity of the films alters with reaction time, temperature and concentration of solutions. Following related Refs. [12–14], a qualitative estimate of the crystallinity is obtained by taking the ratio of the intensity of BST (1 0 1) reflection to that of Ti (0 1 1). According to this criterion, the crystallinity of BST films prepared at different conditions is given in Fig. 2.

From Fig. 2 it is found that the crystallinity of the films altered with time, concentration and temperature. The crystallinity increases along with the increasing temperature and concentration. Along with the increasing of time, the crystallinity increases first, reaches the maximum value and then decreases. Reasons of the decrease of crystallinity at longer time are not very clear now. Preliminary analysis points to side reaction or dissolution of BST films in the mixture of $Ba(OH)_2$ and $Sr(OH)_2$ solution [13,15].

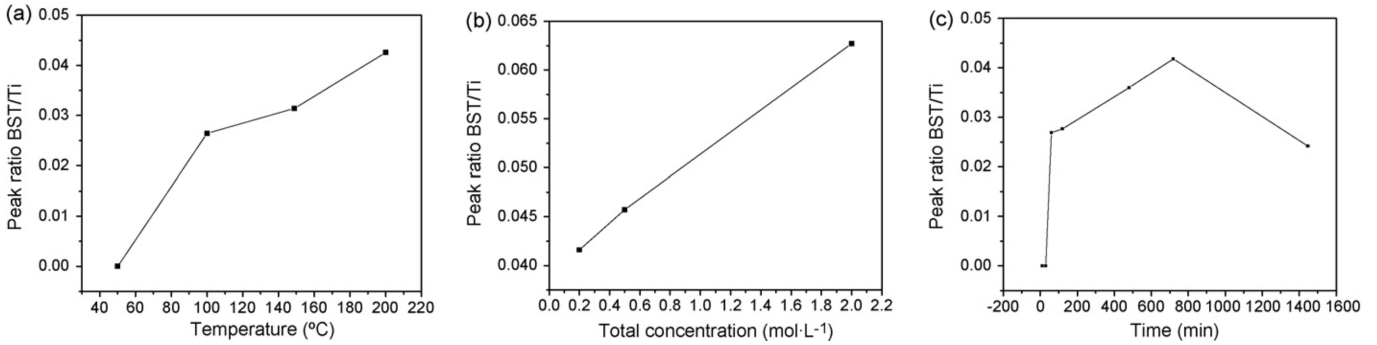

Fig. 2. Crystallinity of BST films at different conditions. (a) Crystallinity vs. temperature; (b) crystallinity vs. total concentration of alkaline earth metal ion; (c) crystallinity vs. reaction time.

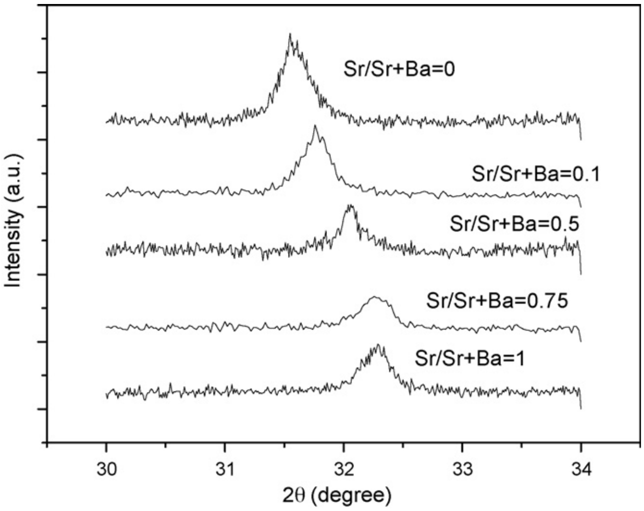

Fig. 3. XRD patterns of (1 0 1) reflections for BST films prepared at different initial ratio of barium and strontium in solution.

3.2. *Effects of the mole ratio of barium and strontium in solution on film composition*

The effects of the initial mole ratio of Ba^{2+} and Sr^{2+} in solution were examined by synthesizing BST films at 200 °C for 12 h in solutions of $Ba(OH)_2$ and $Sr(OH)_2$ with the total concentration of 0.2 M. The mole ratio of Sr/(Sr + Ba) initially in solution varied from 0.0 to 1.0. The film stoichiometry was strongly dependent on the initial ratio of barium and strontium in solution. The (1 0 1) reflection for BST shifted from $BaTiO_3$ toward $SrTiO_3$ as the mole ratio of Ba^{2+} in solution varied from 0 to 1.0 (Fig. 3).

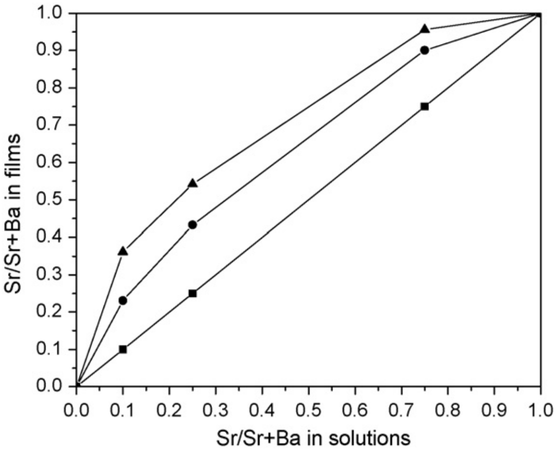

Fig. 4. Effects of mole ratio of barium and strontium in solution on the stoichiometry of BST films (■: suppositional data assuming mole fraction of barium and strontium are same in films and solutions; ●: actual data in 0.2 M solution at 200 °C for 12 h; ▲: actual data in 0.2 M solution at 200 °C for 24 h).

More strontium in the original solution resulted in more strontium in the BST films. But the mole fraction of barium and strontium in BST films was not same as that in the original solution. In order to obtain the mole ratio of barium and strontium in BST films, Vegard's law was adopted here [10,16,17]. The lattice parameters of the hydrothermally derived $BaTiO_3$ and $SrTiO_3$ films were used as end points and were connected by a straight line according to Vegard's law. The composition of each BST film was then estimated using the lattice parameter and the linear fit between the $BaTiO_3$ and $SrTiO_3$ end points (Fig. 4). As it is shown in Fig. 4, there is more strontium in the BST films compared with mole ratio of

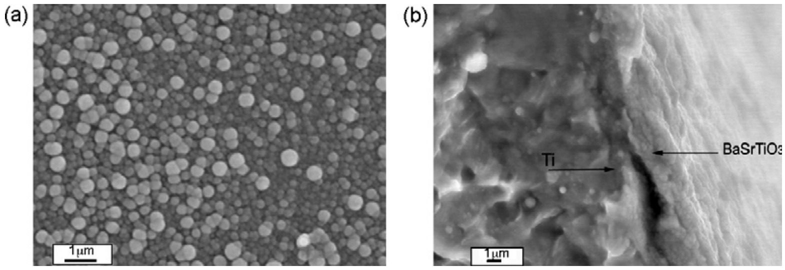

Fig. 5. SEM images of $BaSrTiO_3$ films. (a) Surface and (b) cross-section.

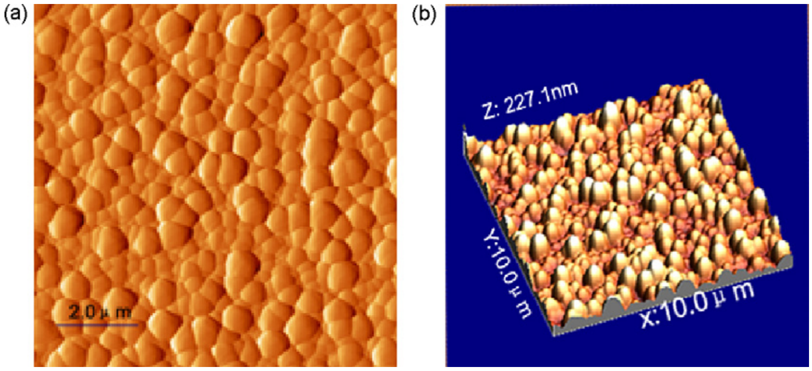

Fig. 6. AFM images of the as-grown $(Ba,Sr)TiO_3$ films. (a) Plane image and (b) stereo image.

strontium and barium in the original solutions except for the solutions containing only barium or strontium ions. Longer reaction time resulted in films with more strontium ratio. The barium contents in the BST films were fairly lower than those in the original solutions. It was in agreement with results of Mccormick and Kajiyoshi on preparation of BST powders by hydrothermal method and hydrothermal preparation of BST films through metal-organic precursor and hydrothermal or electrochemical method [10,16,17]. This indicates that strontium is more readily incorporated into the BST films, relative to barium. The preferred incorporation of strontium into BST films under hydrothermal conditions can be explained by the larger thermodynamic driving forces of formation of $SrTiO_3$ than that of $BaTiO_3$ [17].

3.3. Microstructure of BST films

The SEM images of the surface and cross-section of $(Ba,Sr)TiO_3$ films prepared by the hydrothermal methods are shown in Fig. 5. There are some obvious white particles at the surface. From the energy-dispersive spectroscopy (EDS) of a white particle and nearby particles, we know that the white particle is a Ba-rich phase. Because of the overlap of the Ba and Ti peaks, no accurate composition can be given. The cross-section photographs were obtained by observing mechanically fractured sample. Parts of the film were destroyed by mechanical fracture. The film is highly dense and compact with thickness of 2 μm.

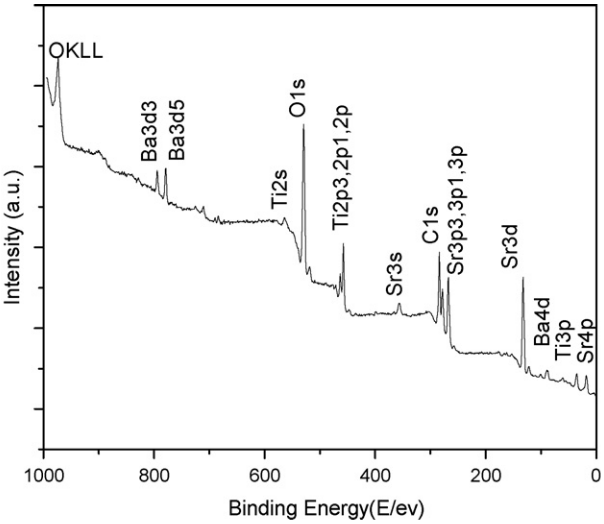

Fig. 7. The wide scan XPS spectrum of the surface of BST films.

The AFM surface topographies of the $(Ba,Sr)TiO_3$ films grown by hydrothermal method are shown in Fig. 6. The film surface is well compacted with $(Ba,Sr)TiO_3$ grains. The root-mean-square (rms) roughness values of this sample which was directly obtained from software supplied by the AFM instrument is about 49 nm. This result is much better than films prepared by similar method reported by other researchers [11].

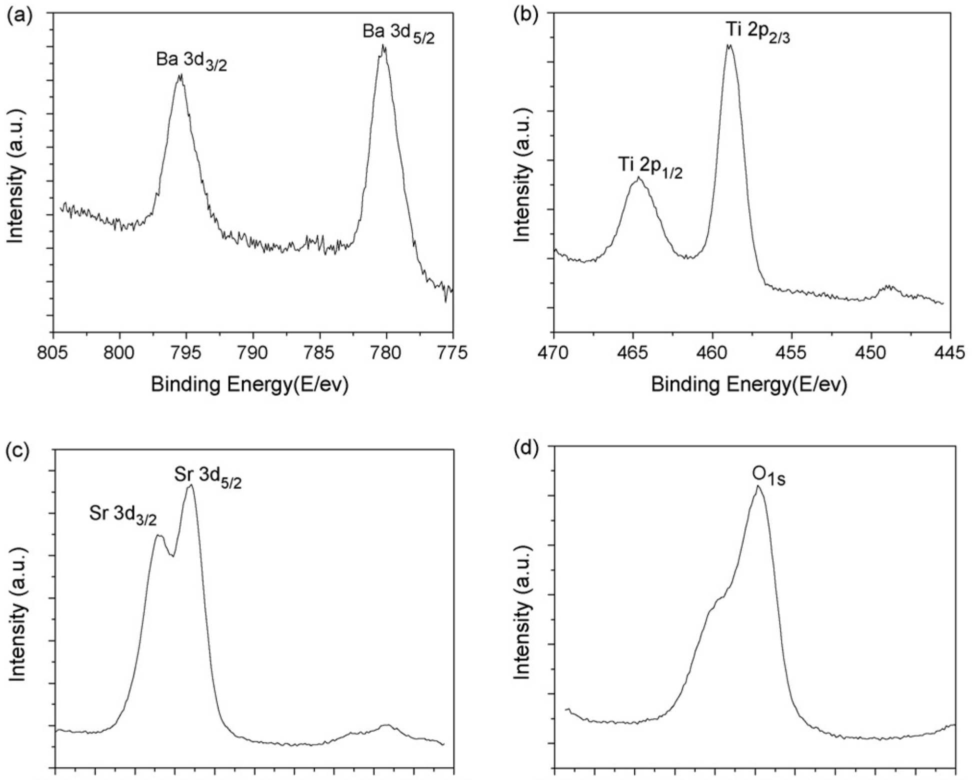

Fig. 8. The narrow-scan of the XPS peaks of Ba (a), Ti (b), Sr (c) and O (d) of BST films.

3.4. XPS analysis

Fig. 7 gives the wide-scan X-ray photoelectron spectrum of the film in the binding energy range of 1000–0 eV. All of the binding energies at various peaks were calibrated using the binding energy of C_{1s}. As shown in Fig. 7, the BST films prepared by hydrothermal method contain Ba, Sr, Ti, O and C elements while carbon may be caused by contamination.

The narrow-scan spectra of the XPS peaks of Ba, Sr, Ti, O elements are given in Fig. 8. The results confirm that the valences of Ba, Sr, Ti and O elements of hydrothermally prepared BST films are +2, +2, +4, and −2, respectively. This is in agreement with the conclusions of Ref. [8]. However, the narrow-scan of oxygen elements shows non-symmetric and broad shape characteristics. It might be due to the existence of OH in the surface of the film [18].

4. Conclusions

$Ba_xSr_{1-x}TiO_3$ (BST) films were prepared under hydrothermal conditions in mixed solutions of $Ba(OH)_2$ and $Sr(OH)_2$. Crystallinity and microstructure of the films changed with time, concentration and temperature. The barium content in the BST films was fairly lower than those in the original solutions. This indicates that strontium is more readily incorporated into the BST films, relative to barium. The results of narrow-scan of XPS spectra confirm that the valences of Ba, Sr, Ti and O elements of hydrothermally prepared BST films are +2, +2, +4, and −2, respectively. AFM analyses reveal that the average surface roughness of the films is 40–50 nm. Uniform and dense BST films of different mole ratio of barium and strontium with thickness up to 2 μm have been prepared successively by the environmentally benign hydrothermal method.

Acknowledgements

This work is supported by the High Technology Research and Development Project, China under Grant Nos. 863-2001AA325010 and 2003AA32G030 and the Ministry of Sciences and Technology of China through 973-Project under Grant No. 2002CB613301.

References

[1] S. Ezhilvalavan, T.Y. Tseng, Mater. Chem. Phys. 65 (2000) 227.
[2] S.B. Majumder, M. Jain, A. Martinez, R.S. Katiyar, J. Appl. Phys. 90 (2001) 896.
[3] Y.-L. Qin, C.-L. Jia, R. Liedtke, R. Waser, K. Urban, J. Am. Ceram. Soc. 86 (2003) 1190.
[4] X. Wei, J. Crystal Growth 286 (2006) 371.
[5] X. Chen, H. Fan, L. Liu, J. Crystal Growth 284 (2005) 434.
[6] J. Zhao, X. Wang, R. Chen, L. Li, Mater. Lett. 59 (2005) 2329.
[7] E. Shi, C.R. Cho, M.S. Jeong, H.J. Kim, J. Mater. Res. 9 (1994) 2914.
[8] Z. Wu, M. Yoshimura, Solid States Ionics 122 (1999) 161.
[9] C.-T. Wu, F.-H. Lu, Thin Solid Films 398/399 (2001) 621.
[10] M.A. McCormick, R.K. Roeder, E.B. Stamovich, J. Mater. Res. 16 (2001) 1200.
[11] D. Gao, D. Xiao, J. Bi, P. Yu, W. Zhang, J. Zhu, Mater. Trans. 44 (2003) 1320.
[12] J. Kajiyoshi, K. Yanagisawa, J. Phys. Condens. Matter 16 (2004) S1351.
[13] R. Bacsa, P. Ravindranathan, J.P. Dougherty, J. Mater. Res. 7 (1992) 423.
[14] H.-Y. Chang, S.-Y. Cheng, C.-I. Sheu, T.-H. Wang, Nanotechnology 14 (2003) 603.
[15] M. Hayashi, N. Ishizawa, S.E. Yoo, M. Yoshimura, J. Ceram. Soc. Jpn. 98 (1990) 930.
[16] R.K. Roeder, E.B. Slamovich, J. Am. Ceram. Soc. 82 (1999) 1665.
[17] K. Kajiyoshi, M. Yoshimura, Y. Hamaji, K. Tomono, T. Kasanami, J. Mater. Res. 11 (1996) 169.
[18] M.E. Pilleux, C.R. Grahmann, V.M. Fuenzalida, R.E. Avila, Appl. Surf. Sci. 65/66 (1993) 283.