Journal of Ceramic Processing Research. Vol. 13, No. 4, pp. 429~431 (2012)

J O U R N A L O F
Ceramic Processing Research

Preparation of $Ca_{0.4}Sr_{0.6}Bi_4Ti_4O_{15}$ templated thin films on NaCl (100) substrates

Su-Hua Fan[a,]*, Ying-Ying Wang[b], Feng-Qing Zhang[b], Yang Chen[b], Peng-Chao Dong[b] and Jun Yin[b]

[a]*Shandong Women's university, jinan, 250300, china*

[b]*School of material science and engineering, Shandong Jianzhu University, jinan, 250101, China*

Free-standing $Ca_{0.4}Sr_{0.6}Bi_4Ti_4O_{15}$ oriented ferroelectric thin films were deposited on water soluble NaCl (100) substrates using a sol-gel method at annealing temperatures ranging from 650 °C to 725 °C. When annealed at 700 °C, the $Ca_{0.4}Sr_{0.6}Bi_4Ti_4O_{15}$ thin film with spherical shaped grains had the smallest strain: 0.2557%. The average size of the spherical shaped grains and surface roughness were close to 100 nm and 1.75 nm respectively.

Key words: Ferroelectric thin film, Soluble substrate, Sol-gel.

Introduction

In recent years, bismuth layer-structured ferroelectrics (BLSFs), especially the four-layer perovskite BLSFs such as $SrBi_4Ti_4O_{15}$ (SBTi), $CaBi_4Ti_4O_{15}$ (CBTi) and $BaBi_4Ti_4O_{15}$ have been intensively investigated due to their good ferroelectric properties [1-4]. Among them, SBTi has a larger remnant polarization and a fatigue-free behavior, but the low Curie temperature ($T_c = 520$ °C) [5] hindered its practical application. Since CBTi with the same structure as SBTi has a high Curie temperature ($T_c = 790$ °C) [6] which fulfills the requirement for higher temperature applications, a series of experiments were carried out on SBTi films by substituting $Sr^{2+}$with Ca^{2+} and it was found that $Ca_{0.4}Sr_{0.6}Bi_4Ti_4O_{15}$ ($C_{0.4}S_{0.6}$BTi) thin films exhibit good ferroelectric properties in our previous work [7].

There are two types of substrates for ferroelectric thin film: one is insoluble such as Si, Pt, fused quartz etc. [8-10], and another is soluble such as NaCl, LiF etc. [11]. However, papers about $Ca_{0.4}Sr_{0.6}Bi_4Ti_4O_{15}$ ferroelectric thin films on soluble substrates are not common. Meanwhile, free-standing oriented ferroelectric thin films (obtained by dissolving the soluble substrate) are desired as templates to induce the bulk, and then better ferroelectric properties were obtained in turn. It is reported that textured $SrBi_2Ta_2O_9$ (SBT) ceramics were fabricated via a templated grain growth (TGG) technique using platelet-like SBT single crystal templates [12]. Towards this goal, we present here preliminary results of efforts towards producing oriented $Ca_{0.4}Sr_{0.6}Bi_4Ti_4O_{15}$ thin films on water soluble substrates-NaCl.

*Corresponding author:
Tel : +531-86526688
Fax: +531-86526786
E-mail: suhuafan@126.com

Experimental details

$Ca_{0.4}Sr_{0.6}Bi_4Ti_4O_{15}$ thin films were deposited on NaCl (100) substrates by a sol-gel method. The precursor solution was prepared by dissolving calcium acetate, strontium acetate, and bismuth nitrate and tetrabutyl titanate in ethylene glycol. Acetylacetone was added to stabilize the solution. Bismuth of 10 mol% excess was added to compensate the bismuth loss during the annealing process. NaCl (100) substrates were used as received (obtained from the Shanghai institute of optics and fine mechanics). The films were deposited onto the substrates by spin coating. Each layer of the films was annealed in a rapid thermal annealing furnace at temperatures ranging from 650 °C to 725 °C in an air atmosphere. The structures of the $Ca_{0.4}Sr_{0.6}Bi_4Ti_4O_{15}$ thin films were investigated by X-ray diffraction (XRD) using a diffractometer (DX-2500, Fangyuan Instru. China) with Cu-Kα radiation ($\lambda = 0.15418$ nm) at a tube voltage of 40 kV and a tube current of 25 mA. The microstructures of $Ca_{0.4}Sr_{0.6}Bi_4Ti_4O_{15}$ thin films were observed by an atomic force microscope (AFM).

Results and discussion

Analysis for lattice match

On one hand, the lattice constant of NaCl ($a = 0.5640$ nm) is close to that of $Ca_{0.4}Sr_{0.6}Bi_4Ti_4O_{15}$ ($a = 0.5428$ nm). According to the following formula, the lattice mismatch between $Ca_{0.4}Sr_{0.6}Bi_4Ti_4O_{15}$ thin films and NaCl substrates is 0.0391. Thus there is a good lattice match between the a-face of perovskite $Ca_{0.4}Sr_{0.6}Bi_4Ti_4O_{15}$ and the NaCl (100) plane, i.e., $Ca_{0.4}Sr_{0.6}Bi_4Ti_4O_{15}$ thin film may show an a-axis preferred orientation:

$$S = \frac{|xa_f - a_s|}{a_f} \quad (x = 1, \sqrt{2}, \sqrt{3}) \qquad (1)$$

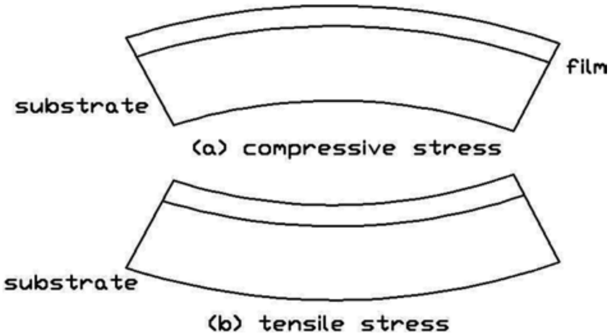

Fig. 1. Schematic diagram for compressive stress and tensile stress between substrate and film.

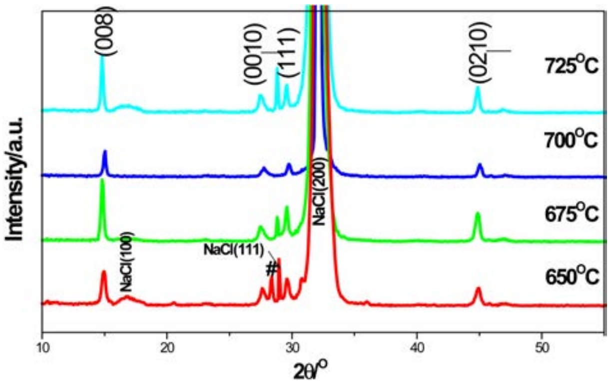

Fig. 2. XRD patterns of $Ca_{0.4}Sr_{0.6}Bi_4Ti_4O_{15}$ thin films on NaCl substrates as a function of annealing temperatures: 650 °C, 675 °C, 700 °C, 725 °C. (The peaks of an unknown phase are masked by #)

where, S is the lattice mismatch between film and substrate, a_f and a_s are the lattice parameters of the film and substrate respectively.

On the other hand, a crystallized $Ca_{0.4}Sr_{0.6}Bi_4Ti_4O_{15}$ thin film on NaCl has a compressive stress [see Fig. 1(a)] on cooling because the thermal expansion coefficient of NaCl ($5.6*10^{-5}$ K) is much higher than that of $Ca_{0.4}Sr_{0.6}Bi_4Ti_4O_{15}$ ($1.5*10^{-5}$ K). Because of the compressive stress, a c-domain orientation of the grains formed on cooling. Therefore, our $Ca_{0.4}Sr_{0.6}Bi_4Ti_4O_{15}$ thin films on NaCl (100) may show a c axis preferred orientation.

However, during the annealing process, some of the grains epitaxially nucleate and grow at the film/ substrate interface. The epitaxial grains in the film on NaCl (100) have a tensile stress [see Fig. 1(b)] because of the smaller lattice constant of $Ca_{0.4}Sr_{0.6}Bi_4Ti_4O_{15}$ (0.5428 nm) compared with that of NaCl (0.5640 nm). The tensile stress may lead to the growth of grains with an a-axis preferred orientation.

Then, a conclusion can be drawn that the orientation of $Ca_{0.4}Sr_{0.6}Bi_4Ti_4O_{15}$ thin film dependents on the three factors discussed above.

XRD analysis

It can be seen from Fig. 2 that characteristic peaks of NaCl and peaks of an unknown phase still exist at lower annealing temperatures (650 °C, 675 °C). The vanishing of NaCl-peaks and the unknown phase-peaks was observed with an increase of the annealing temperature. However, when the film was annealed at higher temperature-725 °C, NaCl-peaks were found. It should be explained that low annealing temperature which can not afford enough energy hinders the forming of the perovskite structure and the homogeneity of nucleation. The higher the annealing temperature, the much closer to the melting point of NaCl crystal, it is the more and more severe thermal motion of Na^+ and Cl^- that has an effect on the forming of perovskite structure and the homogeneity of nucleation. Phase-pure $Ca_{0.4}Sr_{0.6}Bi_4Ti_4O_{15}$ thin films were obtained at 700 °C.

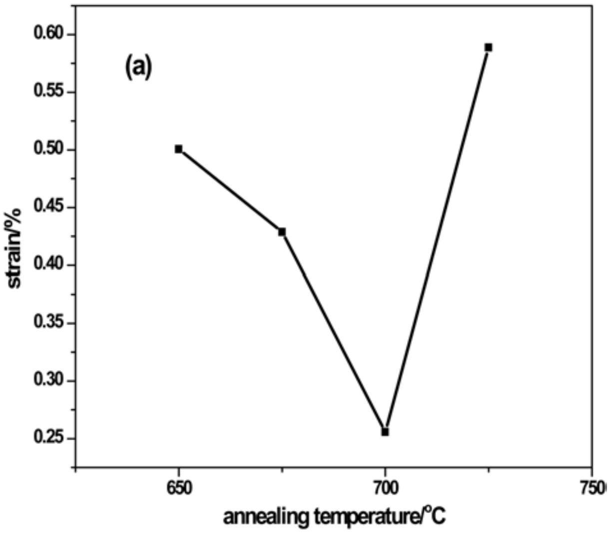

Fig. 3. Annealing temperature dependence on strain of $Ca_{0.4}Sr_{0.6}Bi_4Ti_4O_{15}$ thin films.

It can also be seen that full width at half maximum (FWHM) of the thin film decreases with an increase of the annealing temperature, which in turn indicates that the grain size of the thin film increases. A conclusion can be drawn that when annealed at 700 °C, $Ca_{0.4}Sr_{0.6}Bi_4Ti_4O_{15}$ thin films exhibit a larger grain size. Although $Ca_{0.4}Sr_{0.6}Bi_4Ti_4O_{15}$ thin films annealed at 725 °C have the largest grain size, its phase structure is not pure. It is reported that thin films with a large grain size always exhibit good ferroelectric property. This can be explained by the fact that the large grain facilitates the growth and the inversion of ferroelectric domains and prevents the pinning of the domain walls [13].

The intensity of (00l) peaks decreases and then increases with an increase of the annealing temperature. When annealed at 700 °C $Ca_{0.4}Sr_{0.6}Bi_4Ti_4O_{15}$ thin films have the lowest (00l) peaks, which indirectly indicate that it shows a (b)-axis preferred orientation.

The internal strain of thin films always has an effect on their ferroelectric properties. According to the williamson-Hall formula (*), we can know the internal strain $\Delta d/d$

$$\beta cos\theta = \lambda/D + 4(\Delta d/d) sin\theta \quad (2)$$

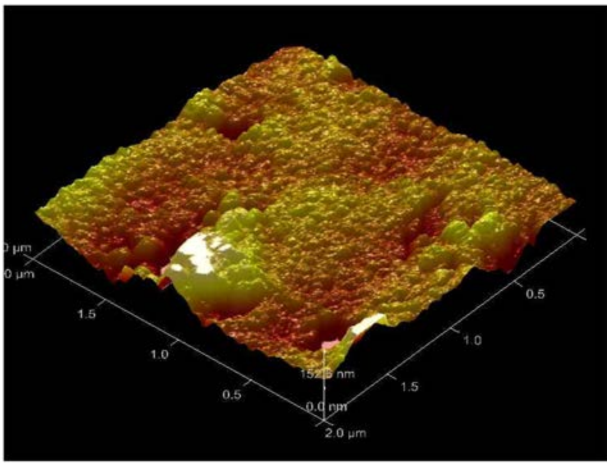

Fig. 4. Morphology of a $Ca_{0.4}Sr_{0.6}Bi_4Ti_4O_{15}$ thin film annealed at 700 °C on a NaCI substrate.

where, β is the FWHM, θ is the angle of diffraction, λ is the wavelength of the diffracted rays, D is the crystallite dimension calculated by the Scherrer formula, and d is the interplanar spacing. The gradient $\Delta d/d$ which represents the internal strain can be obtained by a ploting $\beta\cos\theta - 4\sin\theta$ curve.

Fig. 3 shows the annealing temperature dependence on strain of $Ca_{0.4}Sr_{0.6}Bi_4Ti_4O_{15}$ thin films. A conclusion can be drawn that when annealed at 700 °C $Ca_{0.4}Sr_{0.6}Bi_4Ti_4O_{15}$ thin films exhibit the smallest strain-0.2557%, which has the weakest influence on its ferroelectric properties.

Morphology observation

Considering that the main characteristic peaks [(119) and (200)] of $Ca_{0.4}Sr_{0.6}Bi_4Ti_4O_{15}$ thin films are coincident with NaCl (200), the preferred orientation of thin films would not be determined merely by the XRD pattern. The average grain size and surface roughness of the $Ca_{0.4}Sr_{0.6}Bi_4Ti_4O_{15}$ thin films were estimated using AFM. Fig. 4 shows the morphology of a $Ca_{0.4}Sr_{0.6}Bi_4Ti_4O_{15}$ thin film annealed at 700 °C and it is characterized by a slight surface roughness with a crack-free but not uniform (there are voids among the grains) microstructure. The average size and surface roughness of the spherical shaped grains were close to 100 nm and 1.75 nm, respectively. It is reported [14, 15] that thin films with spherical shaped grains exhibit an a-axis preferred orientation which has a larger remnant polarization than that of thin films with a non-a-axis preferred orientation.

Conclusions

$Ca_{0.4}Sr_{0.6}Bi_4Ti_4O_{15}$ thin films deposited on NaCl (100) substrate exhibits a-axis preferred orientation. When annealed at 700 °C, the $Ca_{0.4}Sr_{0.6}Bi_4Ti_4O_{15}$ thin films with spherical shaped grains have the most pure phase structure, the smallest strain, and larger grain size. It can be predicted that free-standing oriented ferroelectric thin films as the templates can induce the bulk, and then better ferroelectric properties were obtained in turn. However, $Ca_{0.4}Sr_{0.6}Bi_4Ti_4O_{15}$ thin films prepared in our paper were not dense and continuous enough. Thus more effort should be made to improve their crystallization quality.

Acknowledgement

This work was supported by funding from the National Natural Science Foundation of China (50872075) and the Natural Science Foundation of Shandong Province, China (Y2007F36).

References

1. Simoes A Z, Ramirez M A, Riccardi C S, et al, Mater. Lett., 60 (2006) 2020.
2. Kimura M, Sawada T, Ando A, et al, Jpn. J. Appl. Phys. 39 [9B] (2000) 5557-5560.
3. Zeng Jiangtao, Li Yongxiang, Wang Dong,Yin Qingrui, Solid State Commun. 133 (2005) 553.
4. Sim M H, Xue J M, Wang J, Mater. Lett. 58 (2004) 2032.
5. Hirose M, Suzuki T, Oka H et al. Jpn. J. Appl. Phys. 138 [9B] (1999) 5561.
6. Kimura M, Sawada T, Ando A. et al. Jpn. J. Appl. Phys. 139 [9B] (2000) 5557.
7. Fan S H, Xu J, Hu G D, Wang Peiji, Zhang Fengqing, J. Chin. Ceram. Soc. 36 [2] (2008) 237.
8. Ryu S O, Lee W J, Lee W C, Shin W C, You I K, Yu BG, Koo J K, Kim J D, Jpn. J. Appl. Phys. 42 (2003) 1665.
9. Jianming Zeng, Hong Wang, Ming Wang, et al, Thin Solid Films. 322 (1998) 104-107.
10. C. J. Lu, S. B. Ren, H. M. Shen, et al, J. Vac. Sci. Technol. A. 15 [4] (1997) 2167-2172.
11. Stacey W. Boland, Sossina M. Haile, et al, Integrated Ferroelectics. 71 (2005) 59-65.
12. H. Amorı ´n 1, A.L. Kholkin, M.E.V. Costa, et al, Materials Research Bulletin. 43 (2008) 1412-1419.
13. Wen-Hui Ma, Ming-Sheng Zhang, Tao Yu, et al, Overmas Publishers Association. 200 (1997) 109-123.
14. Hu G D., J. Appl. Phys.100 (2006) 096-109.
15. A.Z. Simões, M.A. Ramirez, C.S. Riccardi, et al, Mater. Lett. 60 (2006) 2020-2023.