Journal of Ceramic Processing Research. Vol. 16, No. 5, pp. 511~514 (2015)

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

Electrical properties of predominantly (100)-oriented of Ca^{2+} modified $SrBi_4Ti_4O_{15}$ thin film deposited on $Pt/Ti/SiO_2/Si$ substrates

Fengqing Zhang[a], Pengchao Dong[a] and Suhua Fan[b,*]
[a]*College of Material Science and Engineering, Shandong Jianzhu University, Shandong 250101, China*
[b]*Shangdong Woman University, Shandong 250300, China*

The predominantly (100)-oriented of Ca^{2+} modified $SrBi_4Ti_4O_{15}$ ($Ca_{0.4}Sr_{0.6}Bi_4Ti_4O_{15}$) thin films were fabricated by optimizing the annealing treatment using the metal organic decomposition method. We studied the capacitance-voltage (*C-V*) curve, the dielectric constant (ε) and the dissipation fcator ($\tan\delta$), when the thin film exhibits preferred orientation, especially. The *C-V* curve shows a typical butterfly loop, and the ε, $\tan\delta$ are about 235 and 0.033, respectively. Meanwhile, the *P-E* hysteresis loop as the important characteristic was characterized. The thin film displays a well-saturated *P-E* hysteresis loop with remanent polarization 20.3 $\mu C/cm^2$ and coercive field 132 kV/cm.

Key word: preferred orientation, thin film, dielectric properties, *P–E* hysteresis loop.

Introduction

Interest in lead-free ferroelectric materials arises from their potentially technological applications such as in nonvolatile memories, ferroelectric random access memories (FeRAM) and their environment friendly characteristic. Bi-layered perovskite structured ferroelectric (BLPSF) is one of the most common series, such as $Pb(Zr,Ti)O_3$ (PZT), $SrBi_4Ti_4O_{15}$ (SBT) and $CaBi_4Ti_4O_{15}$ (CBT) thin film [1-3].

BLPSF belongs to the Aurivillius family which have a crystal structure containing interleaved bismuth oxide $(Bi_2O_2)^{2+}$ layers and pseudo-perovskite blocks, denoted $(Bi_2O_2)^{2+}(A_{n-1}B_nO_{3n-1})^{2-}$, where A is mono-, di-, or trivalent ion, with dodecahedral coordination, B is tetra-, penta- or hexavalent ion and n is the number of BO_6 octahedral in each pseudo-perovskite block ($n = 2,3,4,5$) [4, 5]. Among them SBT has larger remanent polarization, but the low Curi Temperature ($Tc = 520$ °C) handicaps its practical use [7]. Recently, higher Curie temperature materials are needed for higher temperature application. While CBT has high Curie temperature ($Tc = 790$ °C), with the same structure of SBT [6]. We tried to combine their advantages by partially replacing Sr^{2+} with Ca^{2+} in SBT thin films and found that doped SBT thin film with a composition $Ca_{0.4}Sr_{0.6}Bi_4Ti_4O_{15}$ (CSBT) exhibits excellent ferroelectric properties [8].

The effect of film orientation on the ferroelectric properties of bismuth layered perovskite compounds has been reported in recent literatures [9-12]. It has been reported that the ferroelectric properties of $SrBi_4Ti_4O_{15}$ and $SrBi_2Ta_2O_9$ thin films in the a-b plane are much better than those along c-axis [13, 14]. Further systematic investigations on the relationship between orientation and polarization for three-layer BLPSF have been done by Hu [9]. However, to our knowledge, few attentions have been paid to the dielectric properties when the four-layer BLPSF thin films exhibit high a-axis preferred orientation. In this work, we prepared the predominantly (100)-oriented CSBT thin film and studied the dielectric properties. The *P–E* hysteresis loop as the important characteristic was also provided to enrich our research.

Experimental

The precursor solution was prepared by dissolving calcium acetate, bismuth nitrate, strontium acetate and tetrabutyl titanate in ethylene glycol at room temperature. Acetylacetone was added to stabilize the solution. 10 mol% excessive bismuth was used to compensate the evaporation of bismuth during the annealing process. The films were deposited on $Pt/Ti/SiO_2/Si$ substrates by spin coating at the speed of 4000 r/m for 30 s. Then the coated film was annealed in a rapid thermal annealing furnace at temperatures ranging from 600 °C to 800 °C for 5 min in an air atmosphere. This process was repeated several times to obtain a certain thickness. A CSBT powder sample was also prepared for comparison by sintering the dried gel derived from the same coating solution. Au top electrodes with a diameter of 200 μm were deposited on CSBT thin films using a sputtering system through a shadow mask for electrical measurements.

The structures of the films and the powder sample

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

were studied by X-ray diffractometer (Bruker D8). The surface of the film that annealed at 800°Ê was detected by a scanning electron microscope (SEM) (JSM-6380LA). A standard ferroelectric tester (Precision Pro. Radiant Tech., Albuquerque, NM) was used to investigate the ferroelectric properties of the CSBT film (T_a = 800 °C). The capacitance-voltage and dielectric properties were measured using an LF impedance analyzer (HP4294A) spectrometer.

Results and Discussion

X-ray diffractometer pattern of CSBT thin films annealed at temperatures ranging from 600 °C to 800 °C and the scanning electron microscope (inset) of CSBT thin film annealed at 800 °C are shown in Figure1. We did not do experiments when the annealing temperature was above 800 °C, for the melting point of bismuth is about 850 °C. The figure has included the CSBT powder data as a contrast. The XRD patterns of films annealed at temperatures ranging from 600 °C to 800 °C match well with that of the powder sample, which exhibit pure perovskite structure. It can be seen that all the films have higher relative intensity of (200) peak [I(200)/I(119)] than that of the powder sample. More important, the relative intensity of (200) peak increases with the increase of T_a from 600 °C to 800 °C. It is worth noting that the relative intensity of (200) peak [I(200)/I(119)] increases up to 3.526 at 800. The result indicates that 800 °C is the optimal temperature for predominantly (100)-oriented CSBT film growth. Meanwhile, we can see that the thin film shows the well crystallization and very dense, uniform by the SEM image shown in the inset of Figure.1. In addition, the thin film is mainly composed of equiaxed grains which have been reported to be the (100)-oriented grains.

Figure.2 shows the *P-E* hysteresis loops of the CSBT thin film annealed at 800 °C under different electric fields at a frequency of 10 kHz. Under the optimal experiment condition, the *P-E* hysteresis loops are well saturated and the value of P_r and E_c are 20.3 μC/cm^2 and 132 kV/cm, respectively. Some work about the relationship between polarization and orientation has been done as mentioned in the introduction. They found that the value of the remanent polarization when the (100)-oriented as the dominance was about two or three times larger than random orientation. They thought that the major polarization direction in part of three-layer or four-layer BLPSF lay along the a-axis. So, the higher of the relative intensity of (100) peak, the better of polarization. Our results confirm this further. Besides, it is found that the hysteresis loops of the film become rectangular for electric fields higher than 240 kV/cm. So, we can concluded that all the results should be ascribed to the well crystallized grains and highly (100) orientation of the films [see Figure.1].

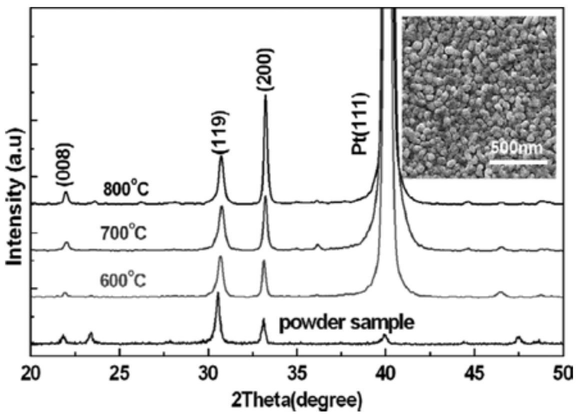

Fig. 1. X-ray diffractometer pattern of CSBT thin films annealed at temperatures ranging from 600 °C to 800 °C and the scanning electron microscope (inset) of CSBT thin film annealed at 800 °C. The CSBT powder sample data as a contrast in the figure.

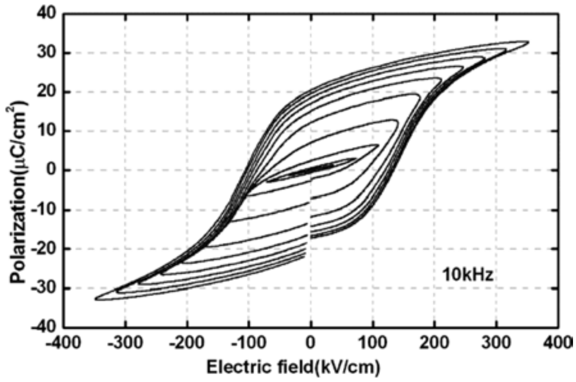

Fig. 2. *P-E* hysteresis loops of the CSBT thin film annealed at 800 °C under different electric fields.

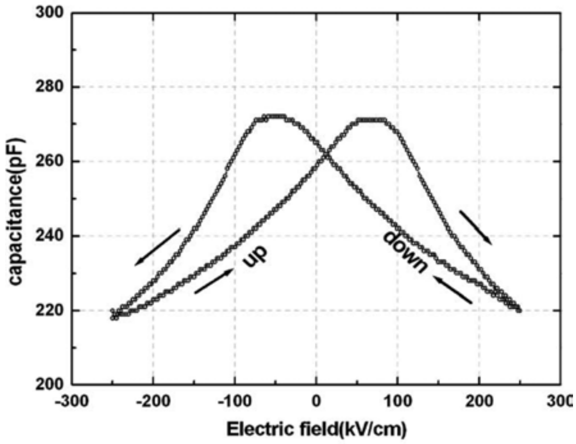

Fig. 3. *C-V* measurement of the CSBT thin film when the annealing temperature was 800 °C.

Variation of capacitance (*C*) with voltage (*V*) is shown in Figure.3. A butterfly loop is observed when the bias voltage is swept between the positive and negative magnitudes. The center of the curve is not located at zero voltage, but shifts slightly toward the

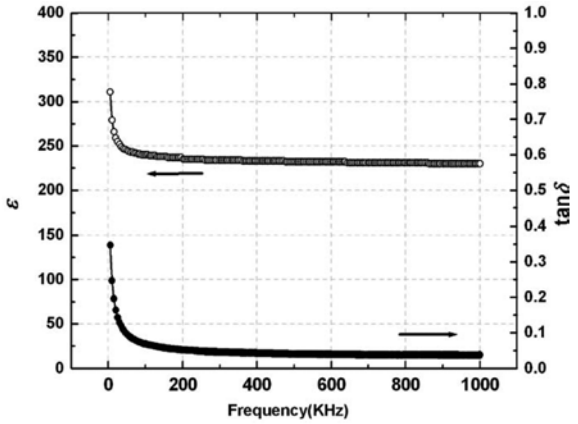

Fig. 4. Frequency dependence of the dielectric constant and the dissipation fator of the CSBT thin film annealed at 800 °C.

positive side. This might be due to lag of polarization with the applied field [15]. The curve coincides with the *P-E* hysteresis loops and the microstructural data [Figure.1 and Figure. 2. The two peaks, which characterize spontaneous polarization switching, are clearly shown in Figure. 3. Also, the curve displays symmetry in the maximum capacitance values that can be observed in the vicinity of the spontaneous polarization switching. This indicates that there is a low concentration of movable ions or charge accumulation at the interface between the dielectric and electrode [16].

Figure.4 illustrates the dielectric constant and the dissipation fcator of the CSBT thin film annealed at 800 °C as a function of the frequency. We can see that the dielectric constant and dielectric loss drop abruptly until the frequency increases up to 15 kHz. Then, although the frequency is increasing, the values yet keep the stable state almost. As shown in the figure, the *å* and tan*ä* are about 235 and 0.033 when they are stable, respectively, which precede over other reported SBT thin films [17, 18]. That may be due to the larger grain size, better crystallinity and less structural defects for our special annealing method.

Conclusions

In summary, if using the special annealing process (combined the layer-by-layer annealing method with the thermal annealing technique), we got predominantly (100)-oriented CSBT thin film by increasing the annealing temperature to 700 °C or 800 °C. The CSBT thin film annealed at 800 °C presented a well-saturated *P-E* hysteresis loop with remanent polarization 20.3 μC/cm^2 and coercive field 132 kV/cm, indicating that the higher of the relative intensity of (100) peak, the better of ferroelectric properties. The *C-V* curve shows a typical butterfly loop which is consistent with *P-E* hysteresis loop and microstructure.

Acknowledgments

This work was supported by funding from National Natural Science Foundation of China (Grant Nos. 51272142, 50872075) and A Project of Shandong Province Higher Educational Science and Technology Program (J15LA05).

References

1. Scott JF, Araujo C.A, "Ferroelectric memories," *Science* 1989, 246, 1400-5.
2. Chung-Hsin Lu, Chung-Han Wu. "Preparation, sintering, and ferroelectric properties of layer-structured strontium bismuth titanium oxide ceramics," *Journal of the European Ceramic Society* 2002; 22:707-714.
3. K. M. Satyalakshmi, M. Alexe, A. Pignolet, N. D. Zakharov, C. Harnagea, S. Senz and D.Hesse, "BaBi4Ti4O15 ferroelectric thin films grown by pulsed laser deposition," *Appl. Phys. Lett.*, 74, 603-5 (1999).
4. E. C. Subbarao, "Crystal Chemistry of Mixed Bismuth Oxides with Layer-Type Structure," *J. Am. Ceram. Soc.*, 45, 166-9 (1962).
5. H.N. Al-Shareef, D. Dimos, T.J. Boyle, W.L. Warren, B.A. Tuttle, "Qualitative model for the fatiguefree behavior of $SrBi_2Ta_2O_9$," *Appl. Phys. Lett.*, 68, 690-2 (1996).
6. K. Kato, K.Suzuki, K. Nishizawa and T. Miki, "Ferroelectric properties of alkoxy-derived $CaBi_4Ti_4O_{15}$ thin films on Pt-passivated Si," *Appl. Phys. Lett.*, 78, 1119-21 (2001).
7. Charles H. Hervoches, Alan Snedden, Richard Riggs, Susan H. Kilcoyne, Pascal Manuel, and Philip Lightfoot, "Structural Behavior of the Four-Layer Aurivillius-Phase Ferroelectrics $SrBi_4Ti_4O_{15}$ and $Bi_5Ti_3FeO_{15}$," *J. Solid State Chem.*, 164, 280-91 (2002).
8. Suhua Fan, Quande Che, Fengqing Zhang, Ran Yu and Hu, Wei, "Enhanced Ferroelectric Properties of Predominantly (100)-oriented $Ca_{0.4}Sr_{0.6}Bi_4Ti_4O_{15}$ Thin Films on Pt/Ti/SiO_2/Si Substrates, " *J. Mater. Sci. Technol.*, 26(11), 981-5 (2010).
9. G. D. Hu, "Orientation dependence of ferroelectric and piezoelectric properties of $Bi_{3.15}Nd_{0.85}Ti_3O_{12}$ thin films on Pt(100)/TiO_2/SiO_2/Si substrates," *J. Appl. Phys.*, 100, 096109-11 (2006).
10. K. Kato, K. Tanaka, K. Suzuki, T. Kimura, K. Nishizawa and T. Miki, "Impact of oxygen ambient on ferroelectric properties of polar-axis-oriented $CaBi_4Ti_4O_{15}$ films," *Appl. Phys. Lett.*, 86, 112901-3 (2005).
11. C. J. Lu, X. L. Liu, X. Q. Chen, C. J. Nie, G. Le. Rhun, S. Senz, and D. Hesse, "Anisotropic ferro- and piezoelectric properties of sol-gel-grown $Bi_{3.15}Nd_{0.85}Ti_3O_{12}$ films with two different orientations on Pt/Ti/SiO_2/Si," *Appl. Phys. Lett.*, 89, 062905-7 (2006).
12. Ho Nyung Lee, Stephan Senz, Alain Pignolet, Dietrich Hesse, "Epitaxial growth of non-c-orientation ferroelectric $SrBi_2Ta_2O_9$ thin films on $SrTiO_3$ substrates," *Journal of the European Ceramic Society.,* 21, 1565-1568 (2001).
13. Hui Sun, Jun Zhu, and Hong Fang, "Large remnant polarization and excellent fatigue property of vanadium-doped $SrBi_4Ti_4O_{15}$ thin films," *J. Appl. Phys.*, 100, 074102 (2006).
14. Dana Miu, J.C. Martinez L, Wiehl , R. Raitieri , H. Adrian, "a-Axis growth of ferroelectric $SrBi_2Ta_2O_9$ thin films on

silicon," *Materials Letters.*, 59, 1243-1247 (2005).
15. Sonalee Chopra, Seema Sharma, T.C. Goel, R.G. Mendiratta, "Electrical and optical properties of sol-gel derived Ca-modified $PbTiO_3$ thin films," *Materials Chemistry and Physics*., 91, 161-165 (2005).
16. A.Z. Simoes, C.S. Riccardi, A. Ries, M.A. Ramirez, E. Longo, J.A. Varela, "Ferroelectric and piezoelectric properties of bismuth layered thin films grown on (100) Pt electrodes," *Journal of materials processing technology.,*I 96, I0-I4 (2008).
17. A.Z. Simoes, M. A. Ramirez, C.S. Riccardi, E. Longo and J.A. Varela, "Effect of oxidizing atmosphere on the electrical properties of $SrBi_4Ti_4O_{15}$ thin films obtained by the polymeric precursor method," *Solid State Sciences.,*10, 1951-1957 (2008)
18. Kenji Takahashi, Muneyasu Suzuki, and Takashi Kojima, "Thickness dependence of dielectric properties in bismuth layer-structured dielectrics," *Appl. Phys. Lett.,* 89, 082901 (2006).