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Processing and characterization of sol-gel deposited (100)-oriented CSBTi thick films on Pt (111)/Ti/SiO_2/Si (100) substrate

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Predominantly (100)-oriented $Ca_{0.4}Sr_{0.6}Bi_4Ti_4O_{15}$ (CSBTi) thick films were deposited on Pt (111)/Ti/SiO_2/Si substrates using a novel powder-gel method combined with annealed procedure. In this method, surface-modified fine CSBTi crystalline particles are well dispersed in a sol-gel precursor solution to have an uniform slurry which is then spin-coated onto a substrate. The thick films were then annealed at 750 °C for the annealing times ranging from 0 h to 4 h. The film annealed for 2 h exhibits a well saturated hysteresis loop with a remanent polarization (P_r) of 28.7 μC/cm^2, much larger than the reported values Furthermore, no discernible fatigue effect can be observed after 10^{10} switching cycles.

Key words: Thin films thickness, Ferroelectric materials, Sol-gels materials processing.

Introduction

Among Ferroelectric films bismuth layer-structured ferroelectric films are of most attractive because of its environmental friendly properties. Recently, $SrBi_4Ti_4O_{15}$ (SBTi) and $CaBi_4Ti_4O_{15}$ (CBTi) which belong to bismuth layer-structured ferroelectrics (BLSFs) have been investigated for the applications in ferroelectric random access memories, high temperature piezoelectric devices, and high-density capacitors [1-6]. BLSFs film has been extensively investigated in its thin film form in order to minimize the operating voltage in micro-device. However, the application based on piezoelectric lms is not limited to the realm of micro-devices. In recent years, there has been increasing interests in integrating ferroelectric thick films on silicon substrate for potential application in micro-electromechanical systems (MEMSs) These applications often require dense and thick micro-patterned films on Si or stainless steel substrates with a thickness of more than 1μm to produce large displacement and generative force. Since CBTi has high Curie temperature (T_c = 790 °C) [7], with the same structure to SBTi, a series of experiments were carried out on $Ca_{0.4}Sr_{0.6}Bi_4Ti_4O_{15}$ (CSBTi) thick films which exhibit good ferroelectric properties with remnant polarization (P_r) of 13.3 μC/cm^2 and coercive field (E_c) of 46.2 kV/cm [8].

In our paper, by applying a novel powder-gel method combined with conventional annealing procedure, the predominantly (100)-oriented CSBTi thick films were successfully deposited on Pt (111) electrodes. . The P_r of the CSBTi films annealed at 750 °C for 2 h is significantly enhanced to 28.7 μC/cm^2.

Experimental

The CSBTi thick films were deposited on Pt/Ti/SiO_2/Si substrates using a novel powder-gel method. The precursor solution was prepared by dissolving calcium acetate, bismuth nitrate, strontium acetate, and tet-rabutyl titanate with stoichiometric ratio in ethylene glycol at room temperature. Acetylacetone was added to stabilize the solution. 10 mol% excessive Bismuth was added to compensate the bismuth loss during the annealing process. Different from conventional sol-gel method, CSBTi (0.5 wt%) nano-powder was added to the original precursor solution to make the slurry more uniform. PVP (2 wt %) was used as dispersing agent. The thick films were deposited onto the substrates by spin coating at 4000 r/m for 30 s. Each layer of the films was pyrolyzed at 400 °C for 3 min in the air. The above processes were repeated till the demanded thickness of the film was obtained. The final thick films were compact and crack-free, with a thickness of about 1.1 μm. Afterwards, the thick films were annealed in the air at 750 °C for annealing times ranging from 0 h to 4 h.

The structures of the CSBTi powder and thick films samples were characterized by X-ray diffraction (XRD). The morphologies of (100)-oriented CSBTi thick films were observed by a scanning electron microscope

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(SEM). Ferroelectric Properties of the films were measured using a standard ferroelectric tester.

Results and Discussion

XRD analysis

As shown in Fig. 1, the detectable diffraction peaks of CSBTi films annealed for 0 h, 1 h, 2 h, and 3 h are in good agreement with those of the powder sample, which indicates that a pure CSBTi phase has formed. The relative intensity of (200) peak [$I_{(200)}/I_{(119)}$] increases with increasing annealing time (T_a) from 0 h to 2 h, as shown in Table 1. However, further increase of Ta leads to the decrease of the relative intensity of (200) peak. Moreover, the secondary phase of pyrochlore can be found in the sample annealed for 4 h. It may be due to the bismuth loss during long time heat treatment. Note that similar structure evolution has been observed in $SrBi_2Ta_2O_9$ thin films deposited on $Pt/Ti/SiO_2/Si$ substrates using sequential layer annealing method [9]. In any case, controlling the growth kinetics and nucleation mechanism is important for the development of an oriented film. Therefore, it can be concluded that the predominantly (100)-oriented BLSF films can be grown by the modified annealing process.

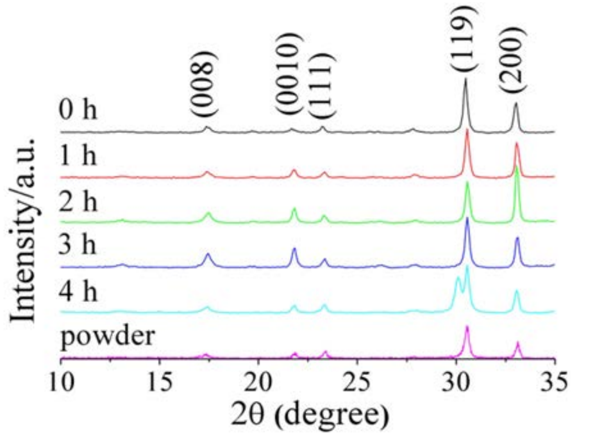

Fig. 1. XRD patterns of CSBTi powder sample and CSBTi thick films annealed at 750 °C with selected annealing time.

Table 1. Structural and ferroelectric properties of CSBTi films as a function of annealing time.

Time/h	$I_{(200)}/I_{(119)}$	$P_r(\mu C/cm^2)$	*Ec(kV/cm)*
0	0.56	17.1	119
1	0.73	20.6	122
2	1.39	28.7	126
3	0.61	17.5	143
4	0.50	12.1	102

SEM analysis

Fig. 2(a)-(e) show SEM micrographs of CSBTi films annealed at 750 °C for different period of time. It is clear that the variation of annealing time can modify the microstructure of the CSBTi thick films. When T_a is more than 2 h, instead of rod-shaped grains, more ball-like grains with 200 nm in diameter were observed in the CSBTi thick films. Besides, it can be seen from Fig. 2(f) that the thick film with a thickness of about 1.1 μm is relatively dense without many cracks and pinholes. For bismuth-layered perovskite films, it has been reported that the ball-like grains have preferentially [100] orientation [10-12]. So the grain of CSBTi thick film annealed for 2 h should be mainly (200)-orientated, which agrees well with the XRD analysis result. While, the grain shape of the thick film with longer Ta becomes plate-like (Fig. 2(e)) and the average grain size is larger than that of the (200)-oriented thick film. This is also consistent with the decrease of (200) peak intensity in XRD data for Ta > 2 h. A strong dependence of ferroelectric and dielectric properties on the film orientation were observed in CBTi ferroelectric thin films with 400 nm-thick [13].

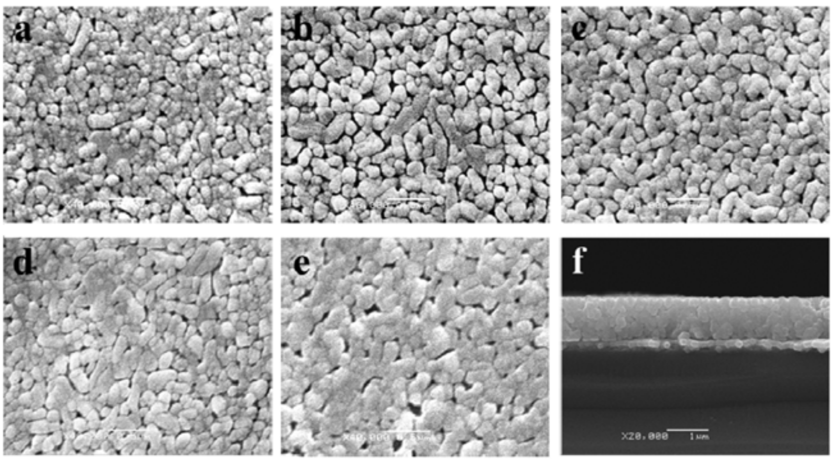

Fig. 2. SEM micrographs of CSBTi films annealed at 750 °C for (a) 0 h, (b) 1 h, (c) 2 h, (d) 3 h, (e) 4 h. And (f) a cross-sectional image of the sample annealed at 750 °C for 2 h.

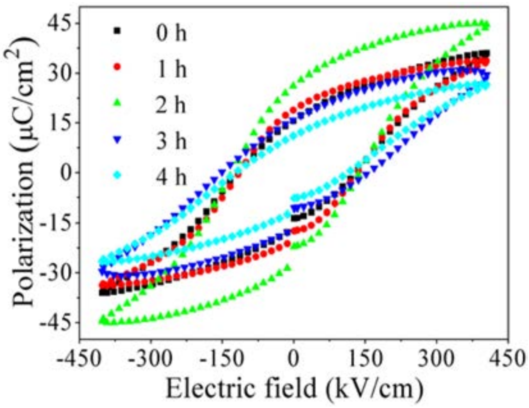

Fig. 3. The *P-E* hysteresis loops of CSBTi thick films annealed at 750 ºC with different period of times.

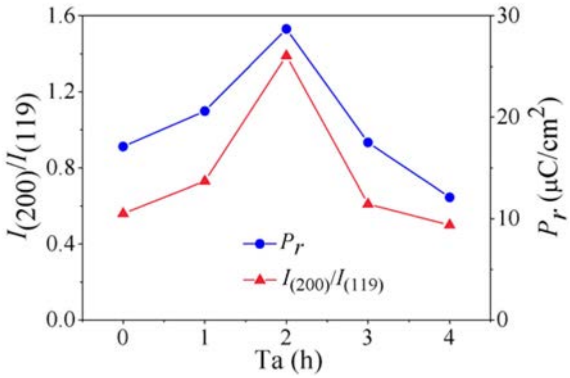

Fig. 4. The relative intensity of (200) peak [$I_{(200)}/I_{(119)}$] and P_r of CSBTi films as a function of annealing times.

P-E Hysteresis loops

Fig. 3 shows the *P-E* hysteresis loops of CSBTi thick films annealed at 750 ºC for different annealing times. It can be seen that the P_r values increase with the increasing of Ta from 0 h to 2 h (see Table 1) and decrease with further increasing of Ta for 2 h to 4 h. Such change of P_r with respect to annealing time are one to one correspondence with the relative intensity change of (200) peak in XRD data, as indicated in Fig. 4. Therefore, the increase of Pr for Ta from 0 h to 2 h is due to the grain growth while the decrease of Pr for 3 and 4 h can be ascribed to the presence of secondary phase caused by bismuth loss during the long time annealing process. The optimized ferroelectric properties at 2 h are mainly resulted from the enhanced *a*-axis oriented crystallization of the CSBTi film. The remanent polarization and coercive field E_c of the predominantly (100)-oriented CSBTi film annealed at 750 ºC for 2 h are 28.7 μC/cm^2 and 126 kV/cm, respectively. To the best of our knowledge, such P_r value in the present work is the largest one for CSBTi films. It is also worth noting that the values of E_c for CSBTi films are about 35.3% of that for CBTi film (= 357 kV/cm) prepared on Pt foil by Kato *et al.* [14]. It is well known that the E_c value of the ferroelectric materials is strongly dependent on the density of domain wall pinning centers. In our case, the annealing temperature is 750 ºC only 120 ºC higher than the Curie temperature (Tc = 630 ºC) of CSBTi. , Therefore, there is weak (or no) driving force for the defects (such as oxygen vacancies) to diffuse into the sample to form the defect dipoles in the paraelectric phase during the annealing treatment [15]. It is natural to expect a low E_c value in the annealed CSBTi thick film.

Ferroelectric properties of the α-axis-oriented CSBTi thick film

To further accurately determine the intrinsic P_r value in 2 h annealed sample, we applied higher electric field in *P-E* loops systematically, as shown in Fig. 5. It can be seen that the hysteresis loops of the film show good rectangularity for the electric field higher than 400 kV/cm [see Fig. 5(a)]. The P_r values are more or less saturated when the electric field is higher than 340 kV/cm. Note that there are still some (001) and (119)-oriented grains in the predominantly (100)-oriented CSBTi thick film annealed at 750 ºC for 2 h. Therefore, the P_r value of the purely *a*-axis-oriented CSBTi film should be higher than 30 μC/cm^2 since the polarization vector of CSBTi is along the *a*-axis. Whatsoever, the high Pr value in our thick film can be ascribed to the

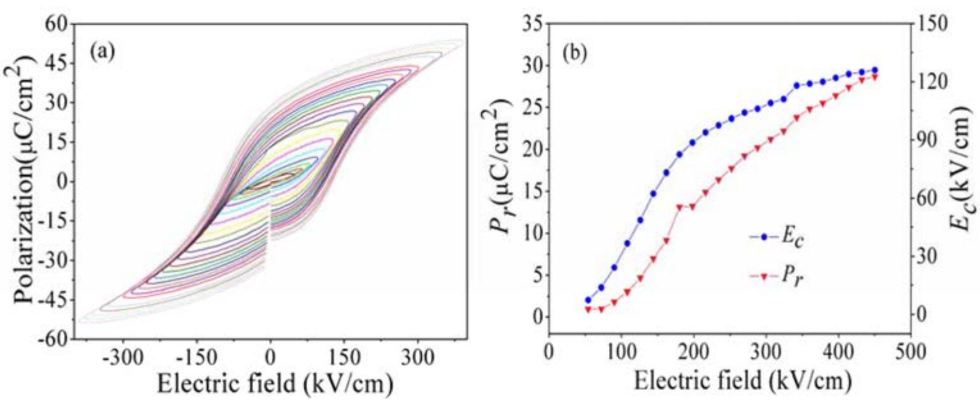

Fig. 5. Ferroelectric properties of the *a*-axis-oriented CSBTi thick film annealed at 750 ºC for 2 h. (a) *P-E* hysteresis loops measured at 10 kHz. (b) The remnant polarization and coercive field as a function of the applied maximum electric fields.

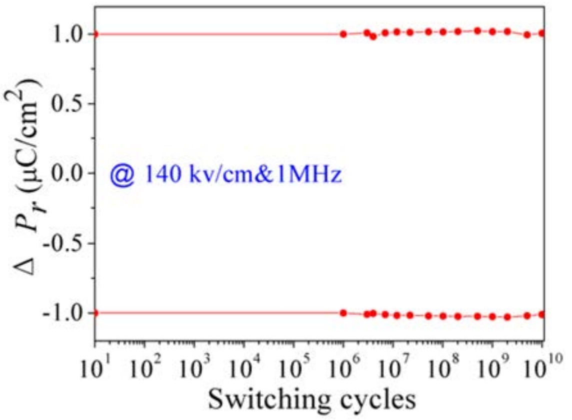

Fig. 6. Fatigue characteristics measured at the electric field of 140 kV/cm and the frequency of 1 MHz for CSBTi thick film annealed at 750 °C for 2 h.

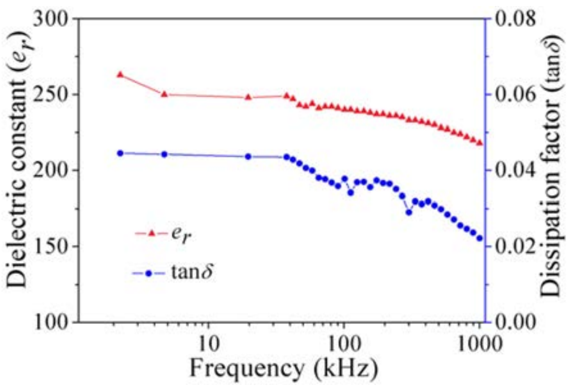

Fig. 7. Dielectric constant and dissipation factor of the thick film annealed at 750 °C for 2 h as a function of frequencies.

predominance of [100] orientation and the well crystallization of the film.

It is worth noting that the CSBTi thick film exhibits excellent fatigue-free characteristics after 10^{10} switching cycles [see Fig. 6]. This may be due to the low concentration of the oxygen vacancies, which have been widely accepted to be the main source of the fatigue behaviors [16-19]. Generally speaking, the formation of the oxygen vacancies depends on the instability of metal-oxygen octahedra in the perovskite structure [20]. Because the metallicity of strontium in the Sr-Ti-O blocks is very stable, it leads to a less concentration of defects and thus prompts the unpinning rate of domain wall [21]. In other words, the more stable the provskite block, the better the fatigue resistance. This result is different from those of 4-layer perovskite BLSF films with excellent fatigue-free characteristics up to 10^{10} switching cycles, which show smaller P_r [5, 22].

Fig. 7 shows the dielectric constant (ε_r) and dissipation factor (tan δ) of the 2 h annealed CSBTi thick film as a function of frequency. The values of ε_r and tan δ at 500 kHz are estimated to be 230 and 0.03, respectively. It can be seen that the dielectric constant decreases slightly with increasing of the frequency. This is due to the fact that some dipoles or domains cannot be switched with ac driving voltage as the frequency increases, which have no contribution to dielectric constants [23]. In contrast, the decrease of tan δ is more obvious at higher frequencies, which may result from the influence of the contact resistance between the sample and the electrode [24]. It may be the grain boundaries which tend to form a parallel conduction path that contribute to the dielectric loss. Also, the density of oxygen vacancies in the perovskite oxide should play a role in the dielectric loss. The mechanism of the dielectric constants and dielectric loss should be investigated in detail further.

Conclusions

In summary, the predominantly (100)-oriented $Ca_{0.4}Sr_{0.6}Bi_4Ti_4O_{15}$ thick films with a thickness of 1.1 μm can be obtained on Pt (111)/Ti/SiO_2/Si substrates using a powder-gel process combined with conventional annealing method. The P_r and E_c of the CSBTi film annealed at 750 °C for 2 h are 28.7 μC/cm^2 and 126 kV/cm, respectively. These excellent ferroelectric properties can be attributed to the predominance of (100) orientation and the good crystallization. No apparent fatigue can be observed after 10^{10} switching cycles in the 2 h annealed CSBTi thick films. Overall, our results suggest that the predominantly (100)-oriented CSBTi thick film grown by powder-gel process combined with conventional annealing method is a promising candidate for the application of MEMSs.

Acknowledgments

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