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Microstructures and electrical properties of $0.5(Ba_{0.7}Ca_{0.3})TiO_3$–$0.5Ba(Zr_{0.2}Ti_{0.8})O_3$ thin films prepared by a sol–gel route

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Abstract

Lead-free $0.5(Ba_{0.7}Ca_{0.3})TiO_3$–$0.5Ba(Zr_{0.2}Ti_{0.8})O_3$ (BCZT50) thin films were deposited on (111)Pt/Ti/SiO_2/Si substrates by a sol–gel route. A $(Pb_{0.8}Ca_{0.2})TiO_3$ (PCT) seed layer was introduced between film and substrate, and found to greatly influence the microstructure and electrical properties of the final BCZT50 films. The BCZT50 film grown without a seed layer showed poor crystallinity with random orientation, while the film with a seed layer was fully crystallized and exhibited high (100) orientation. The BCZT50 film with a seed layer showed enhanced electrical properties compared with of that without a seed layer, including a higher remanent polarization (6.1 μC/cm^2), a larger piezoelectric constant (104 pm/V) and a lower leakage current density ($J < 5 \times 10^{-5}$ A/cm^2). The mechanism of enhancement of electrical properties by use of a seed layer is discussed.

Keywords: A. Films; A. Sol–gel processes; C. Piezoelectric properties; D. $BaTiO_3$ and titanates

1. Introduction

In response to the rising need to protect the global environment, a large number of studies aimed at producing lead-free ferroelectric systems with electrical properties comparable to those of the lead-based ones have been carried out in recent years. Among the many types of lead-free perovskite ferroelectrics, calcium and zirconium co-substituted barium titanate, $1-x(Ba_{0.7}Ca_{0.3})TiO_3$–$xBa(Zr_{0.2}Ti_{0.8})O_3$ (BCZT), is regarded as one of the most promising, because of its excellent dielectric, piezoelectric and ferroelectric properties [1,2]. It is worth noting that the composition of $0.5(Ba_{0.7}Ca_{0.3})TiO_3$–$0.5Ba(Zr_{0.2}Ti_{0.8})O_3$ (BCZT50) is near the morphotropic phase boundary (MPB), and can be considered a solid solution of rhombohedral $Ba(Zr_{0.2}Ti_{0.8})O_3$ and tetragonal $(Ba_{0.7}Ca_{0.3})TiO_3$. Enhanced electrical properties are expected to occur in the MPB region, and many researchers have focused on films near MPB composition [3,4].

As is well known, because of substrate constraint effects and limited thickness, ferroelectric films usually show inferior electrical properties compared with the corresponding bulk ceramics. The film/electrode interface plays an important role in the polarization response of ferroelectric thin films, and properties of the films are greatly degraded by defective material at the film/electrode interface [5]. Thus optimizing the film/electrode interface is crucial to improve electrical properties. In addition, ferroelectric materials have polar axes in certain crystallographic directions; the electrical properties of these films are strongly dependent on their crystal orientation, so orientation of films to the appropriate axis is expected to improve their properties [6]. Many researchers have made great efforts to optimize the film/electrode interface [7,8], and they have also prepared highly oriented ferroelectric films with excellent properties [4,9]. For example, Guo et al. [10] have obtained highly (100)-oriented $BaTiO_3$ film with enhanced dielectric and piezoelectric properties by introducing a buffer layer of

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$LaNiO_3$ between the film and electrode; Jia et al. [11] also reported excellent dielectric properties in highly (100)-oriented $Ba_{0.79}Ca_{0.21}TiO_3$ film deposited on a $LaNiO_3$ buffer layer.

Current research into the $(Ba_{0.7}Ca_{0.3})TiO_3$–$Ba(Zr_{0.2}Ti_{0.8})O_3$ system is mainly concentrated on bulk materials [12,13]; there have been few reports on films with excellent properties, because the corresponding films are difficult to prepare. In our previous study, we found that $(Pb_{1-x-y}La_xCa_y)Ti_{1-x/4}O_3$ films possess a number of useful features, such as low temperature crystallization and a high degree of orientation [14]. Based on these, the aim of the present paper is to prepare high-quality BCZT50 films by introducing a $(Pb_{0.8}Ca_{0.2})TiO_3$ (PCT) seed layer. The effects of the seed layer on microstructure, ferroelectric, piezoelectric and leakage current characteristics of the films will be presented.

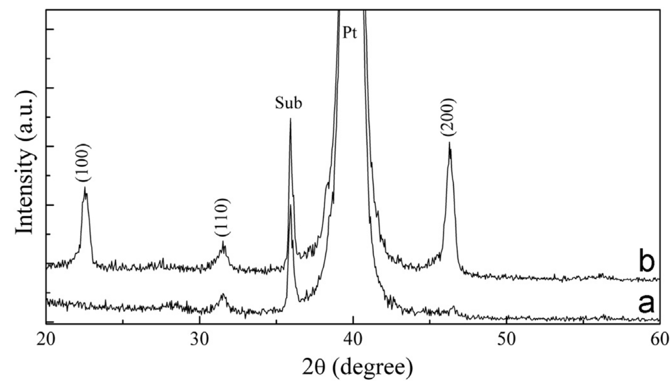

Fig. 1. XRD patterns of BCZT50 films (a) without and (b) with PCT seed layer.

2. Experimental

BCZT thin films were deposited by a sol–gel spin-on technique. Barium acetate, calcium acetate, zirconium *n*-propoxide and titanium isopropoxide were used as the raw materials, and 2-methoxyethanol was the solvent. The solution composition was controlled at a ratio of Ba:Ca:Zr:Ti = 0.85:0.15:0.1:0.9, and the concentration of the final solution of BCZT adjusted to 0.35 M. A PCT solution for the seed layer was also prepared using a similar procedure; the raw materials were lead acetate trihydrate, calcium acetate and titanium isopropoxide. The solution composition was controlled at a ratio of Pb:Ca:Ti = 0.8:0.2:1, and the concentration of PCT solution was adjusted to 0.2 M. The first processing step was to deposit a thin PCT layer onto a $Pt/Ti/SiO_2/Si$ substrate and pyrolyze it at 375 °C for 2 min. The next step was to deposit BCZT layers on top of the PCT coating, and pyrolyzes them at 375 °C for 2 min. The process of spin coating and pyrolyzing were repeated to obtain the desired film thickness of about 450 nm. Finally, the films were annealed at 700 °C for 30 min by conventional thermal annealing in air. The phase composition and orientation were investigated by X-ray diffraction (XRD, Philips, CuKα radiation). The surface morphology was studied by atomic force microscopy (AFM). To measure the electrical properties of the films, dot-type gold electrodes with an area of 3.14×10^{-4} cm^2 were deposited on each BCZT film by magnetron sputtering. Ferroelectric properties and leakage current characteristics were evaluated using a Radiant Precision workstation ferroelectric measurement system. Piezoelectric responses of films were evaluated using a piezoelectric response force microscope with a lock-in-amplifier, and the dielectric properties (measured at 100 Hz) were tested with an Agilent 4294A tester.

3. Results and discussion

Fig. 1 shows the XRD patterns of BCZT50 films annealed at 700 °C for 30 min; the films with and without PCT seed layer have been both crystallized, and show a pure perovskite structure. It must be pointed out that the BCZT50 film with seed layer exhibits much greater crystallinity and highly (100) preferred orientation, while a weak (110) peak is observed in the BCZT50 film without the seed layer. This is because the high (100) orientation of PCT seed layer [14] introduced between the film and substrate adds a large number of nucleation sites, and lowers the nucleation energy, thus the nucleation of BCZT film with seed layer is much easier than that without the seed layer. This ease of nucleation then means that the BCZT film growth tends to follow the crystal plane of PCT seed layer, finally forming highly (100)-oriented BCZT film.

The three-dimensional atomic force microscopy (AFM) images of BCZT50 films with and without a PCT seed layer are displayed in Fig. 2. The grain size of BCZT50 film without seed layer is apparently non-uniform, which is consistent with the lower crystallinity and random orientation of the film. In contrast, the BCZT50 film with seed layer shows denser and finer columnar grains, indicating that the film exhibits good crystallinity and high orientation. The PCT seed layer may act as a template, and can be conducive to improved surface topography, higher crystallinity and oriented grain growth.

Typical *P–E* hysteresis loops of BCZT50 films with and without seed layer are presented in Fig. 3. It is clear that the ferroelectric properties of the BCZT50 film with a seed layer are much better than those of the film without a seed layer. The ferroelectric hysteresis loop of the BCZT50 film without a seed layer shows poor "squareness", with a remanent polarization of 3.5 μC/cm^2; the leakage current characteristics of the film become very obvious when the applied electric field is higher than 400 kV/cm (as shown in Fig. 4a). In contrast, the remanent polarization of the BCZT50 film with seed layer is much greater (*Pr* of 6.1 μC/cm^2), and the *P–E* hysteresis loop of this film is squarer. This *Pr* value is much larger than that of sol–gel-derived BCZT films [9] and is comparable with that of highly (001) textured BCZT ceramics [2]. Another favorable property is that there is no significant leakage current, even if the applied electric field increases to about 600 kV/cm.

Fig. 4 presents the leakage current behaviors of the BCZT50 films with and without a seed layer. It is clear that the leakage current density of the BCZT50 film without a seed layer is much higher than that of the film with a seed layer. For

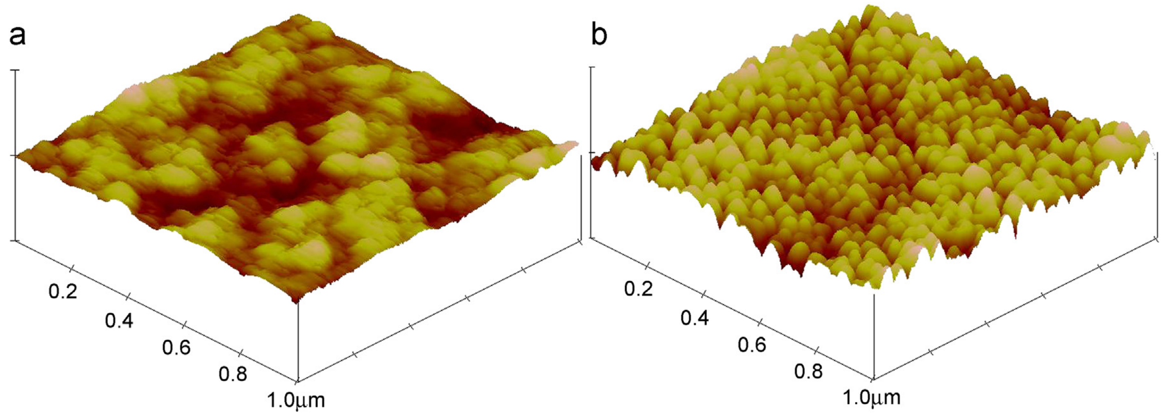

Fig. 2. AFM surface images of BCZT50 films (a) without and (b) with PCT seed layer.

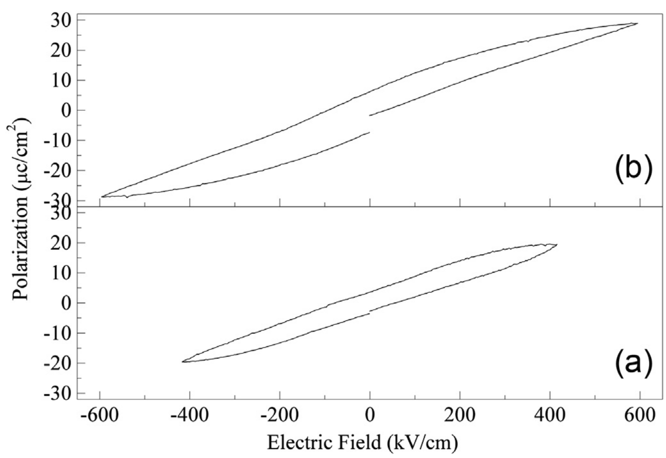

Fig. 3. *P–E* hysteresis loops of BCZT50 films (a) without and (b) with PCT seed layer.

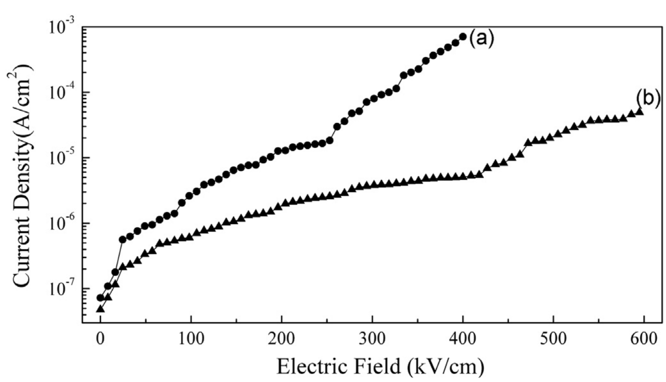

Fig. 4. Leakage current characteristics of BCZT50 films (a) without and (b) with PCT seed layer.

example, when the applied electric field is about 400 kV/cm, the leakage current density of the BCZT50 film without a seed layer has increased to about 7×10^{-4} A/cm^2, while that of the BCZT50 film with a seed layer is only about 5×10^{-6} A/cm^2. This two orders of magnitude difference shows that the leakage current density of the film is effectively reduced by the PCT seed layer. The film with a seed layer shows no substantial leakage current even at an applied electric field of about 600 kV/cm. These differences in leakage current properties are consistent with the differences in ferroelectric properties discussed above.

Table 1
Electrical parameters of BCZT50 films without and with PCT seed layer.

	ε_r	tan δ	*Pr* (μC/cm^2)	d_{33}(pm/V)
BCZT	157	0.037	3.5	62
BCZT/PCT	259	0.024	6.1	104

The dielectric and piezoelectric parameters are presented in Table 1. The dielectric loss is significantly reduced, and the piezoelectric constant increased greatly, when the seed layer is introduced. Notably, the d_{33} value of the BCZT film with a seed layer is larger than that of a (111)-oriented BCZT50 film made via pulsed laser deposition [4].

As we know, the polarization reversal of ferroelectric materials can be achieved by nucleation of new ferroelectric domains at particular nucleation sites and the movement of domain walls [15]. The introduction of the PCT seed layer will generate a large number of nucleation sites for new domains, and in turn make the domain reversals of the film easier, which enhanced the ferroelectric properties and piezoelectric responses of the films. As well as this, optimization of the film/electrode interface means that there will be far fewer vacancies or other point defects resulting from interfacial diffusion between the film and electrode [16]. Meanwhile, the lattice mismatch in film will also be much less, because of the buffering effect of the PCT layer [17]. This in turn decreases the numbers of both pinning centers of domains and charge carriers, which result from defects and lattice mismatch. The lack of defects then makes the nucleation and reorientation of new domains much easier, leading to higher remanent polarization, larger piezoelectric constant, lower leakage current density and lower dielectric loss of the film formed using a seed layer. Enhanced ferroelectric and piezoelectric properties of BCZT50 film with seed layer can also be partly attributed to its highly preferred orientation [18,19]. In our present study, in-plane domain switching of highly (100)-oriented film can continuously occur under applied electric field [20]. Thus the high (100) orientation of the BCZT50 film with a seed layer favors strong ferroelectric properties and piezoelectric response; these results are consistent with the previous report by Lei et al. [21].

4. Conclusions

Highly (100) oriented BCZT50 thin film with a PCT seed layer was achieved by a sol–gel route. The PCT seed layer offers nucleation sites and reduces the activation energy for the crystallization of BCZT50 films, which then form an ideal surface morphology with uniform grains. Because of a perfect film/substrate interface, the highly oriented BCZT50 thin film with PCT seed layer possesses a higher remanent polarization (6.1 μC/cm^2), a larger piezoelectric constant (104 pm/V), a lower leakage current density ($J < 5 \times 10^{-5}$ A/cm^2) and a lower dielectric loss than those of the film made without a seed layer. These results indicate that use of a PCT seed layer is an effective method to obtain highly oriented BCZT films with enhanced electrical properties.

Acknowledgments

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