Low temperature growth of (100)-oriented $\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ - $0.5(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ thin films using a LaNiO_3 seed layer

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Abstract

Low-temperature growth of $\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3$ - $0.5(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ (BZT-0.5BCT) films, at temperatures as low as 550 °C, was successfully achieved by a sol–gel route using a LaNiO_3 seed layer. The influence of the seed layer on the crystallization behavior and electric properties of the films was investigated in detail. It was found that low interfacial diffusion and high (100) orientation were simultaneously achieved by introducing a seed layer between films and substrates. Low leakage current density was obtained as a result of low-temperature crystallization and low interfacial diffusion, and the piezoelectric coefficient remained at a relatively high value because of the high orientation. This study showed that low-temperature

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crystallization suppresses interfacial diffusion and can extend film applications, for example, integrating them with silicon substrates.

Keywords: seed layer; orientation; interfacial diffusion; piezoelectric property.

1. Introduction

The development of memory technology over the past decade has been one of the driving forces behind the tremendous growth in capacitors applications [1-4], and piezoelectric materials with high piezoelectric properties and dielectric properties are extensively applied in sensors, energy harvesters, and infrared detectors [5-7]. Lead-based compounds have been gradually replaced because their wide application has caused many environmental problems. Recently, a significant breakthrough has been made in $\text{Ba}(\text{Zr}_{0.2}\text{Ti}_{0.8})\text{O}_3\text{-}0.5(\text{Ba}_{0.7}\text{Ca}_{0.3})\text{TiO}_3$ (BZT-0.5BCT), which shows a surprisingly high piezoelectric coefficient of $d_{33} \sim 620$ pC/N at the morphotropic phase boundary (MPB), and is considered to be one of the most important lead-free substitutes, with properties that can be comparable to PZT [8,9].

Compared with BCT-0.5BZT ceramics, BCT-0.5BZT thin films possesses several advantages, such as energy harvesting, low driving voltages, and the potential to form integrated circuits with Si [10]. Increasing numbers of researchers have aimed to study BCT-BZT thin films, but investigations of the physical properties of the thin films are rare [11-17]. Wang *et al.* [14] systematically investigated the crystallization temperature of BZT-0.5BCT thin films, and the lowest temperature achieved was found to be 650 °C. Kang *et al.* [15] prepared BZT-0.5BCT thin films from chemical solutions and found that

the complete perovskite phase formed at 700 °C. Luo *et al.* [16] prepared BCZT thin films grown on $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ -buffered Si (001) at temperatures ranging from 550 °C to 810 °C; and found that BCZT thin films start to crystallize at 550 °C and are well crystallized at temperatures above 650 °C. Mimura *et al.* [17] prepared BCZT thin films fabricated on $\text{Pt/TiO}_x/\text{SiO}_2/\text{Si}$ substrates at temperatures above 650 °C, and the temperature at which the films were well crystallized was maintained at approximately 700 °C. Furthermore, for this type of film, more and more researchers have focused on interface issues [18-20]. Chi *et al.* [18,19] conducted an in-depth study of BCT-0.5BZT thin films, in which they synthesized BCT-0.5BZT thin films at 500 °C by introducing $\text{Pb}_{0.8}\text{Ca}_{0.1}\text{La}_{0.1}\text{Ti}_{0.975}\text{O}_3$ as a seed layer, and low interfacial diffusion and high (100) orientation were simultaneously achieved, but the lead-base $\text{Pb}_{0.8}\text{Ca}_{0.1}\text{La}_{0.1}\text{Ti}_{0.975}\text{O}_3$ layer would lead to the environmental pollution. It is well known that, high annealing temperature resulted in serious interfacial diffusion of the thin films and lowers their electrical properties [21,22]. Therefore, it is necessary to obtain thin films with enhanced performance at low-crystallization temperatures.

To increase the crystallization and enhance the piezoelectric property in a BZT-0.5BCT thin film system, this present paper aims to use LaNiO_3 (LNO) as a seed layer, and investigate the impact of this seed layer on crystallization behavior, interfacial diffusion and orientation evolution of BZT-0.5BCT thin films. The piezoelectric properties of the thin films are also investigated.

2. Experimental

BZT-0.5BCT thin films were fabricated via a sol-gel spin-on technique. The precursor sol was synthesized using calcium acetate, barium acetate, zirconium *n* propoxide, and titanium isopropoxide as the raw materials and 2-methoxyethanol as the solvent. The sol concentration of BZT-0.5BCT was adjusted to 0.35 mol/L. LNO solution was used for preparing the seed layer. The raw materials were lanthanum nitrate [La(NO₃)₃] and nickel acetate [Ni(CH₃COO)₂]. La(NO₃)₃ and Ni(CH₃COO)₂ were initially dissolved and refluxed for 30 min in heated 2-methoxyethanol, and the concentration of the solution was adjusted to 0.05 mol/L. The preparation of the precursor solutions was carried out in a glove box in a N₂ atmosphere. The LNO layers were first deposited onto a Pt/Ti/SiO₂/Si substrate and pyrolyzed at 450 °C for 60 s on a hot-plate. The next step was to deposit BZT-0.5BCT on top of the LNO coating and pyrolyze the material at 450 °C for 120 s on a hot-plate. These spin coating and pyrolyzation processes were repeated four times to obtain the final desired film thickness. Finally, the films were separately annealed at 550 °C and 700 °C for 30min in air by Conventional thermal annealing, and the heat rate is 6°C/min. The phase composition of BZT-0.5BCT films was investigated by X-ray diffraction (XRD) using CuKα (λ=1.5406Å) radiation, and the diffractometer was operated at 40 kV and 200 mA. To measure the electrical properties of the films, dot-type gold electrodes with an area of 3.14×10⁻⁴ cm² were deposited onto BZT-0.5BCT films by DC magnetron sputtering. The electric hysteresis loops and leakage current characteristics were evaluated using a Radiant Precision Workstation Ferroelectric Measurement System. The piezoelectric properties of the thin films were

measured by a scanning probe microscopy system under contact atomic force microscopy mode.

3. Results and discussion

XRD patterns of BZT-0.5BCT films without a seed layer (BZT-0.5BCT) and with an LNO seed layer (BZT-0.5BCT/LNO), annealed at 550 °C and 700 °C, are presented in Figure 1. The BZT-0.5BCT films annealed at 550 °C were amorphous, and BZT-0.5BCT films annealed at 700 °C transformed into perovskite structures; furthermore, some pyrochlore peaks were also found in the X-ray diffraction patterns. For the BZT-0.5BCT/LNO thin films, the pure perovskite structure can be successfully achieved at temperatures as low as 550 °C, and the films with the LNO seed layer exhibit high (100) orientation.

X-ray reflectivity (XRR) spectroscopy of BZT-0.5BCT and BZT-0.5BCT/LNO annealed at 550 °C and 700 °C respectively are presented in Figure 2. Compared with other films, the curve of BZT-0.5BCT/LNO thin films annealed at 550 °C oscillates obviously and sharply, which indicates that the interface in the BZT-0.5BCT/LNO thin film is clear, without diffusion. On the contrary, the oscillations in the curve of the pure BZT-0.5BCT thin film annealed at 550 °C and 700 °C disappeared, so this phenomenon demonstrates that the interface in pure BZT-0.5BCT thin films shows severe diffusion. Thus, the accurate modification of the LNO/BZT-0.5BCT thin film system and controlling of the annealing temperature are extremely necessary.

We examined the surface morphologies of BZT-0.5BCT and BZT-0.5BCT/LNO thin

films annealed at different temperatures by the scanning electron microscope (SEM). As shown in Figure 3, it is found that BZT-0.5BCT/LNO thin films annealed at 550 °C and 700 °C exhibits a smooth and crack-free surface, which is composed of densely packed uniform grains. While BZT-0.5BCT thin films 700 °C with 5 nm PLCT seed layer shows a crack surface and uneven grain size (large grains among smaller ones).

The piezoelectric properties characterized by D - V butterfly curves for various types of BZT-0.5BCT films are illustrated in Figure 4. As presented in the D - V butterfly curves, BZT-0.5BCT films with a seed layer possess superior piezoelectric properties compared with those without a seed layer. The butterfly curves of the pure BZT-0.5BCT film annealed at 700 °C have a poor shape, and the maximum displacement (D_{max}) was only 0.44 nm. Compared with pure BZT-0.5BCT film, the D_{max} of the BZT-0.5BCT/LNO thin films anneal at 700 °C increased to 0.98 nm, a well-behaved D - V butterfly curve. Additionally, the obtained value was higher than those of BCZT thin films deposited on Pt/Ti/SiO₂/Si substrates reported by Piorra *et al.* (D_{max} ~0.88 nm) [23]. It is worth noting that relatively good piezoelectric properties (D_{max} ~0.45 nm) were achieved for the BZT-0.5BCT/LNO film annealed at 550 °C; this value is comparable to the maximum values of BZT-0.5BCT films annealed at high temperature (700 °C), and the high piezoelectric properties may be due to the high orientation [24,25]. This also will contribute to the suitability for applications such as integration with a Si- substrate.

Figure 5 depicts the typical leakage current characteristics, where the leakage current of the thin films was shown to be greatly reduced by using the LNO seed layer. The

BZT-0.5BCT/LNO thin film annealed at 550 °C showed a lower leakage current characteristic density compared with the BZT-0.5BCT ($J \sim 1.56 \times 10^{-3}$ A/cm) and BZT-0.5BCT/LNO ($J \sim 2.528 \times 10^{-4}$ A/cm) thin films annealed at 700 °C, as measured at 400 kV/cm. The leakage current of the BZT-0.5BCT film annealed at 700 °C and the BZT-0.5BCT/LNO film annealed at 700 °C gradually increased with increasing electric field, while the leakage current of the BZT-0.5BCT/LNO film annealed at 550 °C reached a gentle steady state. It should be noted that because of the clear interface annealed at a low temperature, the BZT-0.5BCT/LNO film annealed at 550 °C had the lowest leakage current. Meanwhile, compared with pure BZT-0.5BCT thin films and the BZT-0.5BCT/LNO film annealed at 700 °C, the BZT-0.5BCT/LNO film annealed at 550 °C had a mostly symmetric behavior and the value of the leakage current of the film even reached 1.27×10^{-6} A/cm. Generally, by using the seed layer as a substitute for a Pt layer, a potential barrier is expected to form within the interface between the film and electrode, resulting in a reduced leakage current [26,27].

Hysteresis loops measured for the pure BZT-0.5BCT thin film and BZT-0.5BCT/LNO thin films at 1 kHz are shown in Figure 6. As presented in the P - E hysteresis loops, BZT-0.5BCT films with a seed layer have superior ferroelectric properties compared with those without a seed layer. The BZT-0.5BCT/LNO thin films exhibited good saturation, and with increasing annealing temperature, the hysteresis loops became more standardized in shape. The BZT-0.5BCT/LNO film annealed at 550 °C exhibited well-behaved P - E hysteresis loops with maximum remanent polarization ($P_r \sim 6.89$

$\mu\text{C}/\text{cm}^2$), which was higher than those of the BZT-0.5BCT/LNO film annealed at 700°C ($Pr \sim 5.98 \mu\text{C}/\text{cm}^2$) and the BZT-0.5BCT thin film annealed at 700°C ($Pr \sim 4.43 \mu\text{C}/\text{cm}^2$). This value is larger than the value ($Pr \sim 6.64 \mu\text{C}/\text{cm}^2$) reported for a BZT-0.5BCT film prepared on a LNO/Si substrate by Bhardwaj *et al.* [28].

Nucleation is the first step in the growth of a crystalline material and the most important step in the growth of crystalline thin films, which determines the quality of the final film [21,29]. When the LNO seed layer is not applied, no rough surface structures are observed, and there is also no increased nucleus size at the border of the seed layer. In this case, the activation energy for the continuation of growth is much smaller. Such a growth is prone to start from arbitrary defects, which might lead to abnormally large grains among smaller ones, [see Figure. 3(c)], and degrade the electrical properties of the thin film. When LNO is used as seed layer, the introduction of seed layer can form many rough surface structures, which can offer nucleation sites and reduce the activation energy for the crystallization of BZT-BCT films, and make the film anneal at low temperature (550°C). When an electric field is applied, the film switch by the generation of many new reverse domains at particular nucleation sites, which makes the film polarization response easily, thus improves the electric properties.

In addition, precious study reported the LNO seed layer shows (100) orientation [30,31], and leads to the BZT-BCT films in our present study exhibits high (100) orientation. The XRR spectroscopy indicates that the interface in the BZT-0.5BCT/LNO thin film annealed at 550°C is clear, without diffusion. Relatively good piezoelectric

properties ($D_{max} \sim 0.45$ nm) were achieved for the BZT-0.5BCT/LNO film annealed at 550 °C. BZT-0.5BCT/LNO film annealed at 550 °C has a mostly symmetric behavior, the least leakage current density ($J \sim 1.27 \times 10^{-6}$ A/cm), and the maximum remanent polarization ($P_r \sim 6.89$ $\mu\text{C}/\text{cm}^2$). Generally, the BZT-0.5BCT thin film annealed at 550°C exhibits relatively good electric properties, which results from low interfacial diffusion and high (100) -orientation.

4. Conclusions

In the present study, the effects of an LNO seed layer on the orientation and electrical properties of BZT-0.5BCT thin films were investigated. When the annealing temperature was as low as 550 °C, BZT-0.5BCT/LNO thin films crystallized into a perovskite structure and showed high (100) -orientation. The XRR results indicate that low-temperature crystallization can suppress interfacial diffusion and extend film applications by integration with a silicon substrate. This indicates that the BZT-0.5BCT LNO thin film annealed at 550 °C is a good candidate for applications that involve integration with a silicon substrate.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the support of the National Science Foundation of China (51202049, 61172042, 61372013).

References

- [1] P. Muralt, Rep. Prog. Phys. 64 (2001) 1339.
- [2] Y. F. Wang, J. Cui, Q. B. Yuan, Y. J. Niu, Y. Y. Bai, H. Wang, Adv. Mater. 27 (2015)

6658-6663.

- [3] W. W. Yang, Y. S. Yu, L. Wang, C. H. Yang, H. B. Li, *Nanoscale* 7 (2015) 2877-2882.
- [4] Y. S. Yu, A. M. Garcia, B. Ning, S. H. Sun, *Adv. Mater.* 25 (2013) 3090-3094.
- [5] W. Liu, X. Ren, *Phys. Rev. Lett.* 103 (2009) 257602.
- [6] C. W. Ahn, J. J. Choi, J. Ryu, *Mater. Lett.* 141 (2015) 323-326.
- [7] H. X. Tang, Y. R. Lin, H. A. Sodano, *Adv. Energy Mater.* 2 (2012) 469-476.
- [8] B. Su, C. B. Ponton, T. W. Button, *J. Eur. Ceram. Soc.* 21 (2001) 1539-1542.
- [9] X. Z. Shang, Y. Y. Liu, S. Rui, J. M. Guo, T. S. Zhou, G. Chang, Y. B. Yun, *Ceram. Soc.* 41 (2013) 288-291.
- [10] T. Ohno, Y. Kamai, Y. Oda, *Acta Chim. Slov.* 61 (2014) 453-456.
- [11] W. S. Choi, J. Yi, B. Hong, *Mater. Sci. Eng. B* 109 (2004) 146-151.
- [12] D. S. Keeble, F. Benabdallah, P. A. Thomas, *Appl. Phys. Lett.* 102 (2013) 092903.
- [13] H. Bao, C. Zhou, D. Xue, *J. Phys. D Appl. Phys.* 43 (2010) 465401.
- [14] Z. M. Wang, K. Zhao, X. L. Guo, W. Sun, H. L. Jiang, *J. Mater. Chem. C* 1 (2012) 522-530.
- [15] G. Q. Kang, K. Yao, J. Wang, *J. Am. Ceram. Soc.* 95 (2012) 986-991.
- [16] B. C. Luo, D. Y. Wang, M. M. Duan, *Appl. Surf. Sci.* 270 (2013) 377-381.
- [17] K. I. Mimura, T. Naka, T. Shimura, *Thin Solid Films* 516 (2008) 8408-8413.
- [18] Q. G. Chi, C. H. Zhang, J. Sun, *J. Phys. Chem. C* 118 (2014) 15220-15225.
- [19] Q. G. Chi, X. Wang, W. L. Li, *Appl. Phys. Lett.* 98 (2011) 242903.
- [20] Q. G. Chi, J. Sun, C. H. Zhang, *J. Mater. Chem. C* 2 (2013) 172-177.

- [21] W. L. Li, Q. G. Chi, W. D. Fei, J. Am. Ceram. Soc. 94 (2011) 1503-1508.
- [22] M. L. Calzada, I. Bretos, R. Jiménez, Adv. Mater. 16 (2004) 1620-1624.
- [23] A. Piorra, A. Petraru, H. Kohlstedt, Appl. Phys. 109 (2011) 104101.
- [24] W. Gong, J. F. Li, X. C. Chu, Acta Mater. 52 (2004) 2787-2793.
- [25] B. C. Luo, D. Y. Wang, M. M. Duan, Appl. Phys. Lett. 103 (2013) 122903.
- [26] W. C. Hu, C. R. Yang, X. B. Liu, W. He, X. Z. Tang, J. Mater. Sci. Mater. electron. 19 (2008) 61-66.
- [27] J. F. Jia, K. Huang, Q. T. Pan, J. Sol-gel Sci. Techn. 42 (2007) 9-12.
- [28] C. Bhardwaj, B. S. S. Daniel, D. Kaur, J. Phys. Chem. Solids 74 (2013) 94-100.
- [29] J. Fu, Y. Cong, J. Li, B. Luan, C. Y. Pan, Y. M. Yang, B. Y. Li, Y. C. Han, Macromolecules 37 (2004) 6918-6925.
- [30] W. L. Li, T. D. Zhang, D. Xu, Y. F. Hou, W. P. Cao, W. D. Fei, J. Eur. Ceram. Soc. 35 (2015) 2041-2049.
- [31] W. L. Li, T. D. Zhang, Y. F. Hou, Y. Zhao, D. Xu, W. P. Cao, W. D. Fei, Rsc Adv. 4 (2014) 56933-56937.

Figure Captions

Figure. 1. XRD patterns of BZT-0.5BCT and BZT-0.5BCT/LNO annealed at 550 °C and 700 °C respectively.

Figure. 2. XRR spectroscopy of BZT-0.5BCT and BZT-0.5BCT/LNO annealed at 550 °C and 700 °C respectively.

Figure. 3. Surface morphologies of (a) BZT-0.5BCT/LNO annealed at 550 °C, (b) BZT-0.5BCT/LNO annealed at 700 °C, and (c) BZT-0.5BCT annealed at 700 °C.

Figure. 4. *D-V* butterfly curves BZT-0.5BCT and BZT-0.5BCT/LNO annealed at 550 °C and 700 °C respectively.

Figure. 5. Leakage current characteristics of BZT-0.5BCT and BZT-0.5BCT/LNO annealed at 550 °C and 700 °C respectively.

Figure. 6. The hysteresis loops of BZT-0.5BCT and BZT-0.5BCT/LNO annealed at 550 °C and 700 °C respectively.

Highlights

► Low interfacial diffusion and high (100) orientation of BZT-BCT films were simultaneously achieved ► Low leakage current density was obtained due to low-temperature crystallization and low interfacial diffusion. ► Piezoelectric coefficient of films remained at a relatively high value.

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5

Figure 6