

Effects of film thickness and preferred orientation on the dielectric properties of $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$ films

L Z Cao¹, W Y Fu¹, S F Wang², Q Wang³, Z H Sun¹, H Yang¹,
B L Cheng¹, H Wang³ and Y L Zhou^{1,4}

¹ Beijing National Laboratory for Condensed Matter Physics, Institute of Physics, Chinese Academy of Sciences, Beijing 100080, People's Republic of China

² Physics and Technology College, Hebei University, Baoding 071002, People's Republic of China

³ Electronic Materials Research Laboratory, Key Laboratory of the Ministry of Education, Xi'an Jiaotong University, Xi'an 710049, People's Republic of China

E-mail: ylzhou@aphy.iphy.ac.cn

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Abstract

$(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$ (BZN) films with different thicknesses and preferred orientations have been fabricated on Nb doped SrTiO_3 substrates by pulsed laser deposition. As the thickness increases, the permittivity increases, and the dielectric loss decreases, while the tunability only has a little variation. The asymmetric behaviour of the electric field dependent permittivity reduces gradually with the increasing thickness, which should be attributed to the decrease in the effect of the interfacial layer between the dielectric film and substrate (electrode). Furthermore, compared with the (1 0 0) oriented BZN film, BZN film with (1 1 1) preferred orientation exhibits high dielectric loss.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

In recent years, there has been great interest in the application of dielectric materials for tunable microwave devices, such as phase shifters, filters and resonators. In the practical tunable device applications, several critical requirements should be satisfied, which include low dielectric loss, adequate tunability, low leakage current and moderate permittivity [1]. Among the tunable materials, $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ (BST) has been extensively investigated for its large tunability [2, 3]. However, the large dielectric loss in the microwave region of BST film prevents it from further application [4]. Currently, a cubic pyrochlore phase $(\text{Bi}_{1.5}\text{Zn}_{0.5})(\text{Zn}_{0.5}\text{Nb}_{1.5})\text{O}_7$ (BZN) is attracting much attention as a new tunable material due to its low dielectric loss in the microwave region [5, 6]. Many researchers have made efforts to grow BZN thin films and explored its application in microwave devices [5, 7–10]. Most of these efforts were

limited to the growth of polycrystalline BZN films with a certain thickness. In practical applications, it is well known that thickness and orientation have great influence on the microstructure and dielectric properties of the films. However, research work on these influences on BZN films has not been carried out systemically until now.

Recently, we have fabricated the *c*-axial oriented BZN thin film and the BZN/BST heterolayered film by pulsed laser deposition (PLD) on 1% Nb doped SrTiO_3 substrate (STON) [11, 12]. Based on the above work, in this paper, we reported the fabrication of (1 0 0) oriented and (1 1 1) oriented BZN films with different thicknesses by PLD on STON substrates, and further investigation of the dependence of dielectric properties on both the thickness and orientation of the films is underway. It was observed that the dielectric constant increases and the dielectric loss decreases with the increasing film thickness, while the tunability only varies slightly. Besides, the asymmetric behaviour in the electric field

⁴ Author to whom any correspondence should be addressed.

dependent permittivity reduces gradually with the increasing thickness, which is attributed to the decrease in the effect of the interfacial layer between the dielectric film and substrate (electrode). Furthermore, BZN film with (111) preferred orientation exhibits higher permittivity, dielectric loss and tunability than the (100) oriented films.

2. Experiments

Conventional ceramic processing was used to prepare the BZN ceramic target for PLD experiment [13]. (001) and (110) STON single crystals were chosen as substrates (Hefei Kejing Mater. Tech. Co., Ltd, China), and they served as the bottom electrode directly due to their metallic conductivity at room temperature. A 308 nm XeCl excimer laser with laser energy density of about 2 J cm^{-2} was used to ablate the ceramic target. BZN thin films were grown at 700°C in 30 Pa of O_2 by the PLD method, followed by a post-annealing process at 550°C for 20 min in 1 atm O_2 .

The thicknesses of the films were measured by scanning electron microscopy (SEM). The crystal structures of the BZN films were analysed by x-ray diffraction (XRD, Mac Science M18AHF) using $\text{Cu K}\alpha$ radiation with a scan step of 0.01° . The surface morphologies of the BZN films were observed with a Nano Scope IIIa-D3000 atomic force microscopy (AFM) via tapping mode. Dielectric measurements were performed on an Agilent 4294A precision impedance analyser, using a parallel-plate capacitor structure with a 120 nm thick Pt top electrode.

3. Results and discussion

Figure 1 shows the XRD patterns for BZN films with different thicknesses and substrates. The BZN films deposited on (001) STON substrates show a c -axial preferred growth, while the one deposited on (110) STON substrate shows a preferred growth in the (111) orientation. Based on Lotgering's theory, the orientation factor can be defined as

$$F = (P - P_0)/(1 - P_0), \quad (1)$$

$$P = \sum I_{(abc)} / \sum I_{(hkl)}, \quad (2)$$

where F denotes the orientation factor with respect to a reference plane (abc), where (abc) denotes the Miller indices, P is for the textured thin film and means the ratio of the sum of intensities of the interested reflections of planes (abc) to the sum of all reflections and P_0 stands for the equivalent ratio for ceramic powder of the target with random orientation. The value of the orientation factor for preferred orientation is in the range 0 to 1. $F = 0$ denotes a film with random orientation, while $F = 1$ denotes an epitaxial film [14]. The orientation factors of the films are listed in table 1.

We obtain $F \geq 0.75$ for the BZN films deposited on the (001) STON substrates, which exhibits a c -axial preferred growth. The preferred growth may be due to the small lattice mismatch between BZN films and (001) STON substrates when the latter is rotated to an angle of 45° [12]. The BZN film deposited on the (110) STON substrate exhibits a preferred growth in (111) orientation. Here the (111) oriented growth of the BZN film is governed by the principle of minimum

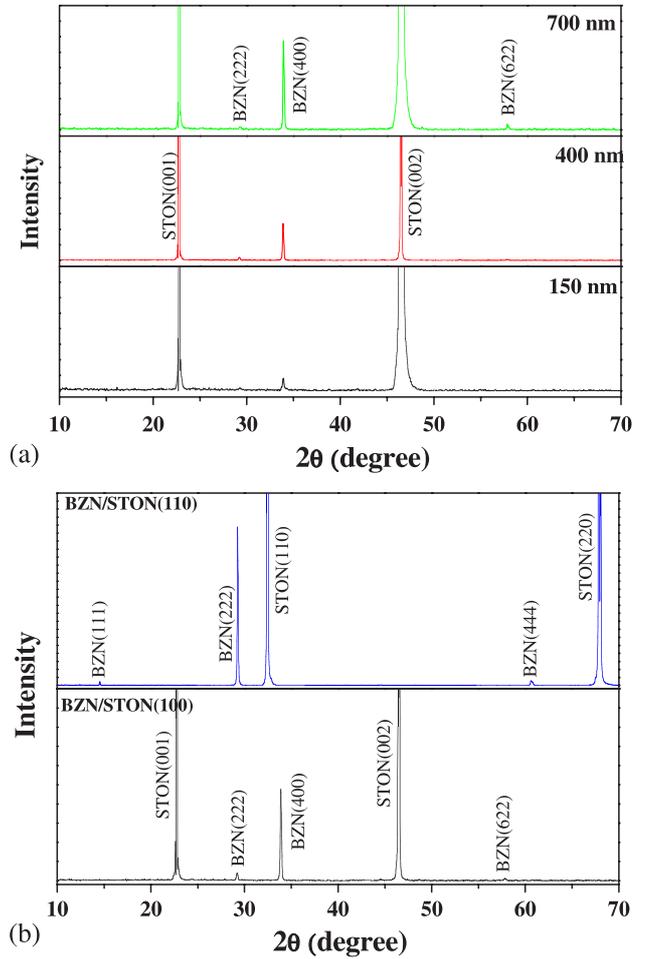


Figure 1. XRD patterns of BZN films grown on STON substrates with (a) different thicknesses, (b) different preferred orientations.

energy considering the (111) plane is the close-packed one in cubic structure.

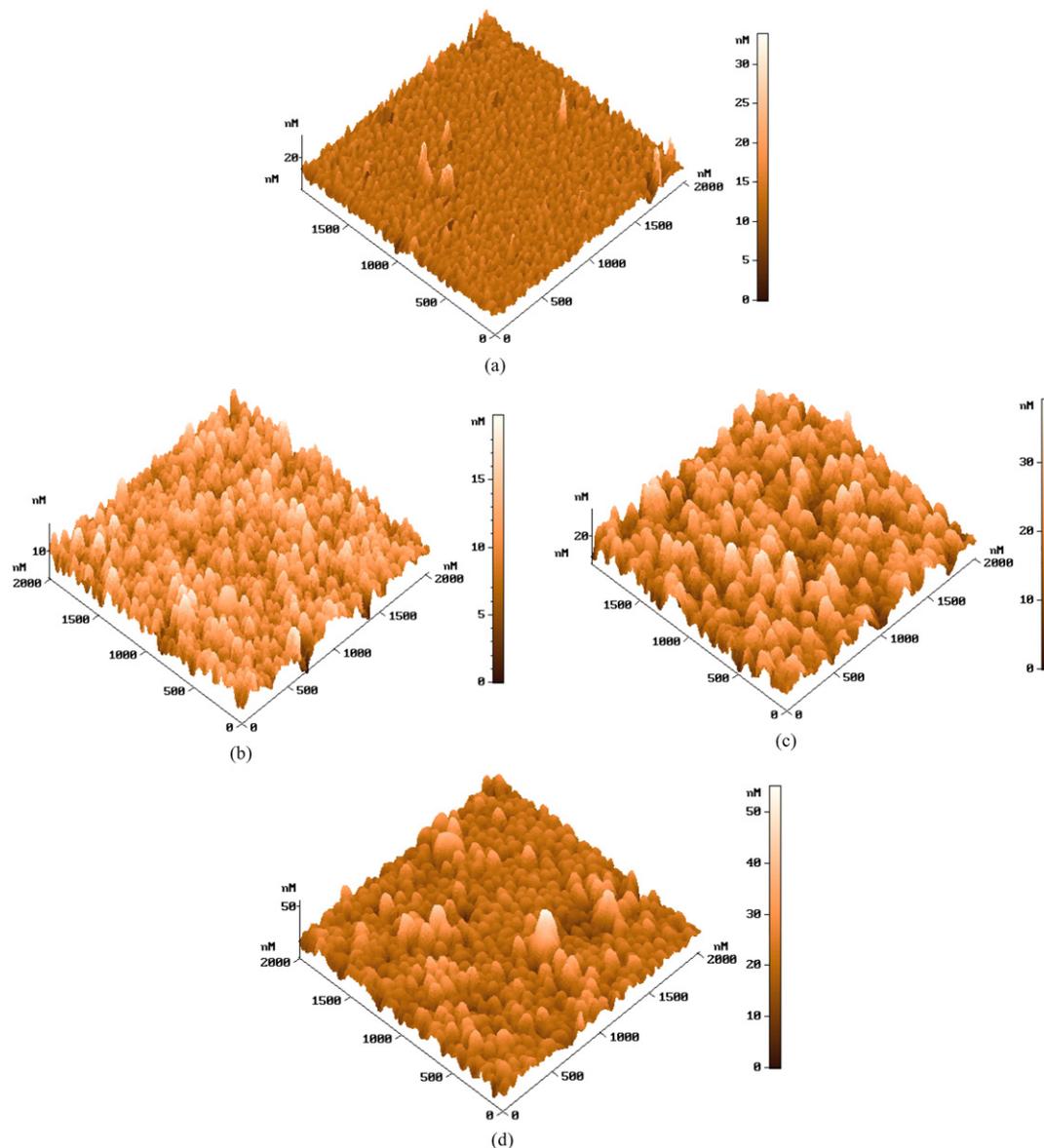
As listed in table 1, the orientation factor of the thicker film is higher than that of the thinner one for c -axial oriented BZN films. In the case of thinner films, the biaxial compressive stress induced by the lattice mismatch between film and substrate plays a negative role in the c -axial preferred growth of the BZN film. As the film grows thicker, the stress caused by the mismatch releases gradually, exhibiting an increased preferred oriented growth.

Figure 2 shows the AFM images of the BZN films. The root mean square (RMS) roughness and the estimated grain size of the BZN films are listed in table 1. The results reveal that the grain size and the RMS of the films increase with increasing thickness. Increased grain size of the film is often associated with the improvement of crystal behaviour, which agrees with the XRD result. Moreover, the grain size and the RMS of the (111)-axial oriented BZN film are in a reasonable value range compared with that of c -axial oriented BZN with the same thickness.

Figure 3 shows the permittivity and dielectric loss as a function of frequency measured in the range from 100 kHz to 1 MHz with an ac oscillation voltage of 400 mV. The permittivity almost keeps a constant value, while the loss tangent increases obviously with the increasing frequency

Table 1. Summary of texturing coefficient, grain size and RMS for the BZN thin films.

	Thickness	150 nm	400 nm	700 nm	400 nm
BZN films	Preferred orientation	<i>c</i> -axial orientation	<i>c</i> -axial orientation	<i>c</i> -axial orientation	(1 1 1) orientation
	Orientation factor	0.75	0.78	0.84	0.98
	Grain size	50 nm	60 nm	80 nm	75 nm
	RMS	1.9 nm	2.6 nm	5.7 nm	5.2 nm

**Figure 2.** AFM images of (a) 150 nm thick, *c*-axis oriented, (b) 400 nm thick, *c*-axis oriented, (c) 700 nm thick, *c*-axis oriented, (d) 400 nm thick, (1 1 1) preferred oriented, BZN films.

for both the BZN films. Such an increase in loss tangent accompanied by a constant value of permittivity should be attributed as the conductor losses contribution to the metallic electrode [8]. Furthermore, the permittivity is 70, 119 and 122 for the 150 nm thick, 400 nm thick and 700 nm thick BZN films at the frequency of 100 kHz, respectively. The permittivity of the 150 nm thick film is about 50 lower than that of the other

two samples, and the permittivity increases and then tends to a certain value with increasing film thickness. It is well known that there exists an interfacial layer between the dielectric film and substrate. The interfacial layers are generally low permittivity layers and can reduce the effective permittivity of the film due to series connection with the actual dielectric layer. It is suggested that the effect of interfacial layer on the

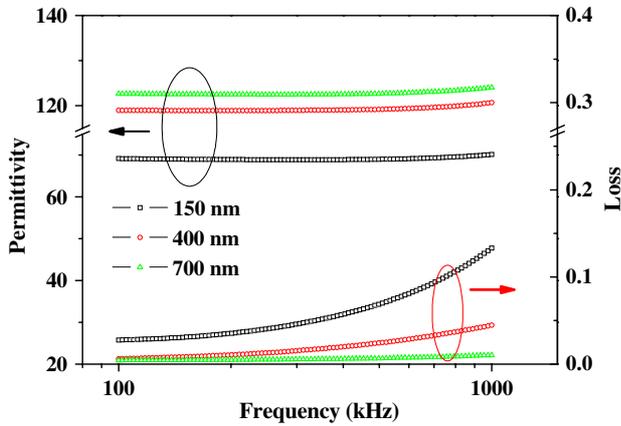


Figure 3. Frequency dependent permittivity and loss tangent of the *c*-axis oriented BZN films.

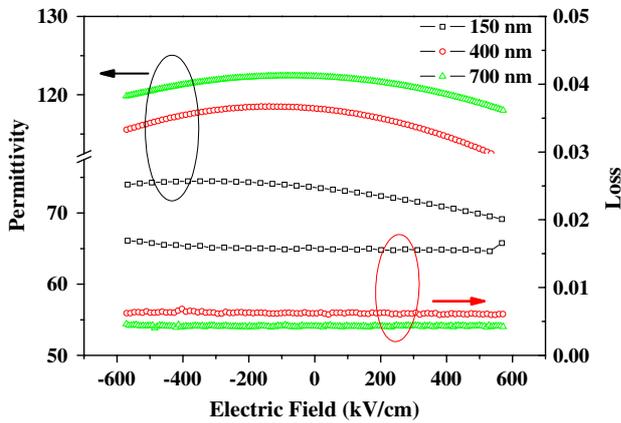


Figure 4. Bias electric field dependent permittivity and loss tangent of the BZN (100) preferred oriented films.

permittivity is more pronounced for the thinner films, and it becomes weak as the films become thicker.

In addition, the dielectric loss decreases gradually from 0.01 to 0.004 with increasing thickness from 150 to 700 nm at the frequency of 100 kHz. The reason for the dielectric loss of the 150 nm thick film being much larger than that of the other two samples may be due to its high dielectric leakage current and poor crystal structure. It should be noted that the 700 nm thick BZN film exhibits dielectric loss below 0.01 in the range from 100 kHz to 1 MHz, and its low dielectric loss is very attractive for practical tunable device applications.

Figure 4 gives the bias field dependent permittivity and dielectric loss of the BZN films measured at the frequency of 100 kHz. For all samples, dielectric loss keeps a constant value with bias electric field. Under an electric field of 570 kV cm^{-1} , tunability of the 400 nm thick and 700 nm thick BZN films is 5% and 4%, respectively. And the tunability of the 150 nm thick film can still reach 5% in spite of its low permittivity, which may be attributed to the larger electric field applied to the dielectric layer of the whole BZN film (two equivalent capacitors which are in in-series connection). A figure of merit (FOM) is used to characterize the dielectric properties of the

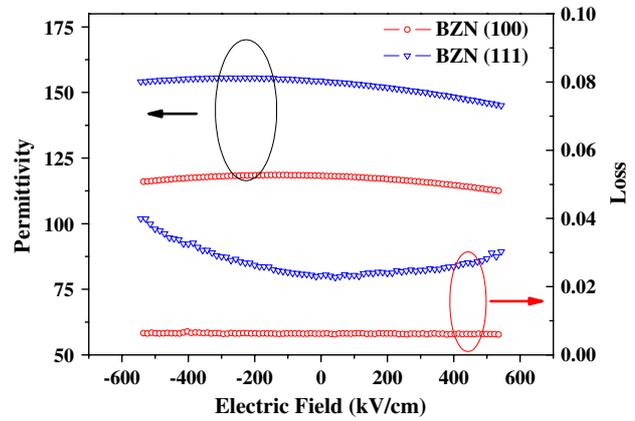


Figure 5. Bias electric field dependent permittivity and loss tangent of the 350 nm thick BZN films with (100) and (111) preferred orientations.

films:

$$\text{FOM} = \left(\frac{\text{tunability}}{\tan \delta} \right) = \left\{ \frac{[\varepsilon(0) - \varepsilon(E_{\max})]/\varepsilon(0)}{\tan \delta} \right\}, \quad (3)$$

where $\varepsilon(0)$ and $\varepsilon(E_{\max})$ are the permittivity of the BZN films measured at zero and maximum bias fields, respectively. A FOM of 10 is achieved for the 700 nm thick BZN (100) sample due to its lower dielectric loss. The FOM of the 150 nm thick and 300 nm thick BZN films with (100) preferred orientation is 5 and 8, respectively.

It should be noted that the bias electric field E_m at which the permittivity has its maximum value is not located at zero bias electric field, but shifts towards the negative bias region. Moreover, the curve becomes more and more symmetrical with increasing thickness. Such asymmetric behaviour may result from the asymmetry of the top and bottom electrodes [12]. As mentioned above, an interfacial layer exists between the dielectric film and substrate (electrode). The permittivity here is the contribution of two capacitors which are in in-series connection, i.e. dielectric film and interfacial layer. The effect of interfacial layer on the permittivity is more pronounced for the thinner films. With increasing film thickness, such an effect becomes less pronounced, and finally the asymmetric behaviour of the curves disappears.

The dielectric properties of the BZN films with different preferred orientations are shown in figure 5. Firstly, asymmetric behaviour caused by the asymmetry of top and bottom electrodes was also observed in the film with (111) preferred orientation. Moreover, BZN film with (111) preferred orientation shows high permittivity, dielectric loss and tunability of 155, 0.02 and 6.5%. Ito *et al* investigated the dependences of dielectric properties on (111) and (100) orientations for $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ films grown on (100)SrRuO₃|| (100)SrTiO₃ and (111)SrRuO₃|| (111)SrTiO₃ substrates, respectively, and found that the films with (111) orientation had larger permittivity, dielectric loss and tunability than those with (100) orientation [15]. They attributed this to the effect of strain applied to the $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3$ films from the substrate. Here, the difference of permittivity, dielectric loss and tunability in BZN films with different preferred orientations may be also related to the influence of stress caused by the

mismatch of film and substrate. The detailed mechanism of this phenomenon will be investigated in our further work.

4. Conclusion

(Bi_{1.5}Zn_{0.5})(Zn_{0.5}Nb_{1.5})O₇ thin films with different thicknesses and preferred orientations have been deposited on STON substrate by pulsed laser deposition, and dependence of the dielectric properties on the thickness and orientation of the films has been investigated. As the thickness increases, the dielectric loss decreases and the permittivity increases, while the tunability only has a little variation. The asymmetric behaviour of the electric field dependent permittivity reduces gradually with increasing thickness, and it is considered to be related to the effect of the interfacial layer between the dielectric film and substrate (electrode). Compared with the (1 0 0) BZN film with the same thickness, the (1 1 1) oriented BZN film exhibits higher dielectric loss which may be associated with stress caused by the mismatch between the BZN film and STON substrate.

Acknowledgments

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Reference

- [1] Cole M W, Joshi P C and Ervin M 2001 *J. Appl. Phys.* **89** 4413
- [2] Jin F, Auner G W, Naik R, Schubring N W, Mantese J V, Catalan A B and Micheli A L 1998 *Appl. Phys. Lett.* **73** 2838
- [3] Ngo E, Joshi P C, Cole M W and Hubbard C W 2001 *Appl. Phys. Lett.* **79** 248
- [4] Ha S, Lee Y S, Hong Y P, Lee H Y, Lee Y C, Ko K H, Kim D W, Hong H B and Hong K S 2005 *Appl. Phys. A—Mater.* **80** 585
- [5] Ren W, Trolier-McKinstry S, Randall C A and Shrout T R 2001 *J. Appl. Phys.* **89** 767
- [6] Wang H, Elsebrock R, Waser R and Yao X 2005 *Ferroelectrics* **327** 33
- [7] Hong Y P, Ha S, Lee H Y, Lee Y C, Ko K H, Kim D W, Hong H B and Hong K S 2002 *Thin Solid Films* **419** 183
- [8] Lu J W and Stemmer S 2003 *Appl. Phys. Lett.* **83** 2411
- [9] Park J, Lu J W, Stemmer S and York R A 2005 *J. Appl. Phys.* **97** 084110
- [10] Kim J Y, Kim D W, Jung H S and Hong K S 2005 *Japan. J. Appl. Phys.* **44** 6648 Part 1
- [11] Fu W Y, Cao L Z, Wang S F, Sun Z H, Wang Q, Wang H and Cheng B L 2006 *Appl. Phys. Lett.* **89** 132908
- [12] Cao L Z, Fu W Y, Wang S F, Sun Z H, Wang Q, Yang H, Wang H and Cheng B L 2007 *J. Phys. D: Appl. Phys.* **40** 1460
- [13] Wang H and Yao X 2001 *J. Mater. Res.* **16** 83
- [14] Lotgering F K 1959 *J. Inorg. Nucl. Chem.* **9** 113
- [15] Ito S, Takahashi K, Okamoto S, Koutsaroff I P, Cervin-Lawry A and Funakubo H 2005 *Japan. J. Appl. Phys.* **44** 6881 Part 1