

# The effects of the $\text{LaNiO}_3$ interlayer in the preferential orientation and the dielectrical properties of $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$ thin films

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**Abstract**  $\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$  (BST) thin films were grown on different substrates with or without  $\text{LaNiO}_3$  (LNO) layer by a modified sol–gel process. The BST thin films obtained have full perovskite phase with dense and crack-free surface. BST thin films on different substrates with LNO layer show (100) preferential orientation, the texture coefficient (TC) value is calculated to be about 42.7%, whereas those without LNO layer show a fairly reduced preferential orientation, the TC value is just about 24.8%. It is considered that the preferential orientation is induced by the interface stress between LNO and BST. Electrical property measurements showed that BST thin film with a LNO interlayer has lower capacitance and larger dielectric loss, which is due to smaller grains of the thin film.

**Keywords** BST thin film · Sol–gel method · Preferential orientation · LNO

## 1 Introduction

$\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$  (BST) ( $0 \leq x \leq 1$ ) is a solid solution ferroelectric material exhibiting high dielectric constants, low dielectric loss, high dielectric breakdown strength, and a large dielectric constant change with applied dc electric field. It has recently received considerable attention as a promising candidates for application in dynamic random access memories (DRAMs) and tunable microwave devices [1–3].

In recent years, conductive oxide layers such as  $\text{SrRuO}_3$ ,  $\text{IrO}_2$ ,  $\text{LaNiO}_3$  (LNO),  $\text{RuO}_2$ , and  $\text{LaAlO}_3$  have been studied intensively due to their potential application for bottom electrode or buffer layer in deposition perovskite thin films. Among of these, the LNO have attracted some attention as a conducting layer for applications in ferroelectric memories. It has been confirmed that LNO, replacing Pt electrode, significantly improves the microstructure and the electrical property of ferroelectric thin films [4–6].

According to some reports, textured BST thin films always grow on single crystal LNO (100) substrate [7], but the mechanism of preferential orientation is not very clear [8]. To explore the possible mechanism, we studied the different preferential orientation phenomenon of BST thin film deposited on different substrates with or without LNO layer. The texture coefficients were calculated and possible mechanisms were proposed.

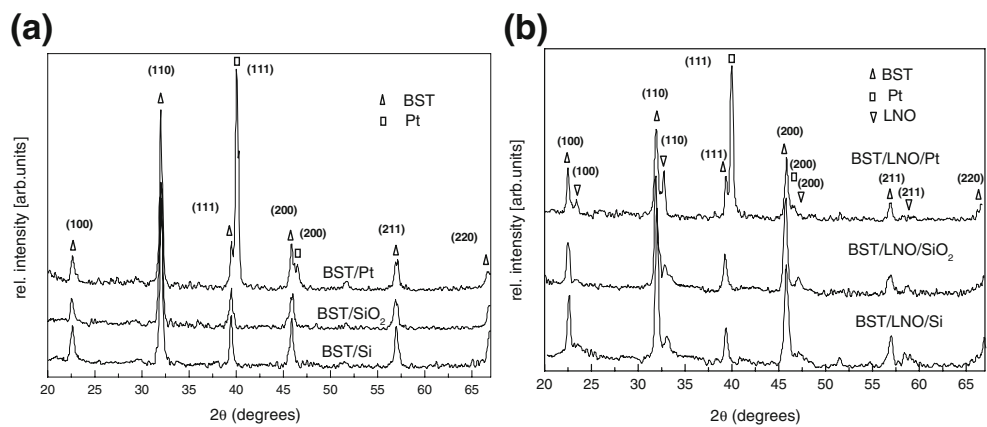
## 2 Experimental

Lanthanum nitrate ( $\text{La}(\text{NO}_3)_3$ ) and nickel acetate ( $\text{Ni}(\text{Ac})_2$ ) were used as starting materials for synthesizing the LNO precursor solution. They were dissolved in methoxyethanol (MOE) with heating and stirring and mixed in a molar ratio of  $\text{La}/\text{Ni}=1:1$ . The concentration of the resulting solution was adjusted to 0.25 M for optimum film deposition. The BST thin films were fabricated by a modified sol–gel method.  $\text{Ba}(\text{Ac})_2$ ,  $\text{Sr}(\text{Ac})_2$ , and  $\text{Ti}(\text{OC}_4\text{H}_9)_4$  were used as the raw materials. Details of the process are described elsewhere [9].

Thin films were deposited by spin-coating method on three kinds of substrates: Si (100) (brief as Si below),  $\text{SiO}_2/\text{Si}(100)$  (brief as  $\text{SiO}_2$  below), and  $\text{Pt}/\text{Ti}/\text{SiO}_2/\text{Si}$  (brief as Pt below). Two types of BST thin films were prepared. In type

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**Fig. 1** XRD patterns of BST thin films deposited on different substrates (a) without LNO interlayer and (b) with LNO interlayer



1 film, BST thin films were deposited directly on the substrate without a LNO interlayer. For type 2 film, LNO thin film were deposited firstly on the substrate and crystallized, then BST thin films were deposited on to it. All the as-deposited films were finally annealed at 700°C for 20 min to promote crystallization.

The crystallization behavior, the surface morphology and the dielectric properties of the thin films were studied by using Rigaku D-MAX<sup>o</sup>C X-ray diffractometer (XRD), JEOL 6700F field emission scanning electron microscopy (FESEM), Digital Instruments NanoScope <sup>o</sup>C a atomic force microscopy (AFM) and HP4192A impedance analyzer.

**3 Results and discussion**

Figure 1(a) shows the XRD patterns of BST thin films prepared on different substrates without LNO layer (type 1). As seen in Fig. 1(a), The 2-theta diffraction angles and relative intensity of the XRD peaks of BST thin film are found to agree with the perovskite phase. The BST thin films had been crystallized with random orientation. The crystalline behavior of the thin films deposited on different substrates are almost the same. Figure 1(b) shows the XRD patterns of BST thin films deposited on different substrates

with LNO layer (type 2). It is found that they are also well crystallized with perovskite phase. The relative intensity of (100) and (200) peaks are stronger than the corresponding peaks shown in Fig. 1(a), indicating the type 2 thin film have (100) preferential orientation.

The texture coefficient (TC) value corresponding to the (100) orientation for different thin films were estimated according to the peak intensity in the XRD patterns by using the following formula: [10]

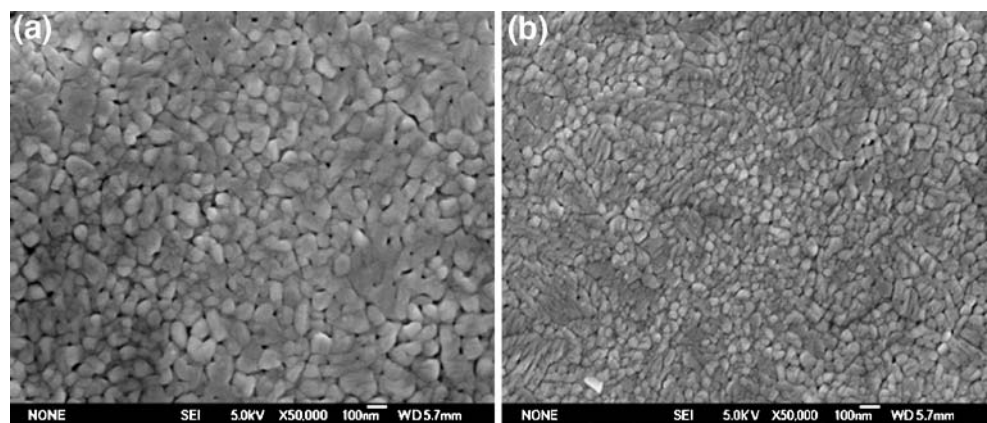
$$TC_{HKL}(\%) = \frac{NA - 1}{N - 1} \times 100\%$$

in which,  $A = \frac{1}{1 + \sum_{H'K'L'} \frac{I_{HKL}^* / I_{H'K'L'}^*}{I_{HKL} / I_{H'K'L'}}$

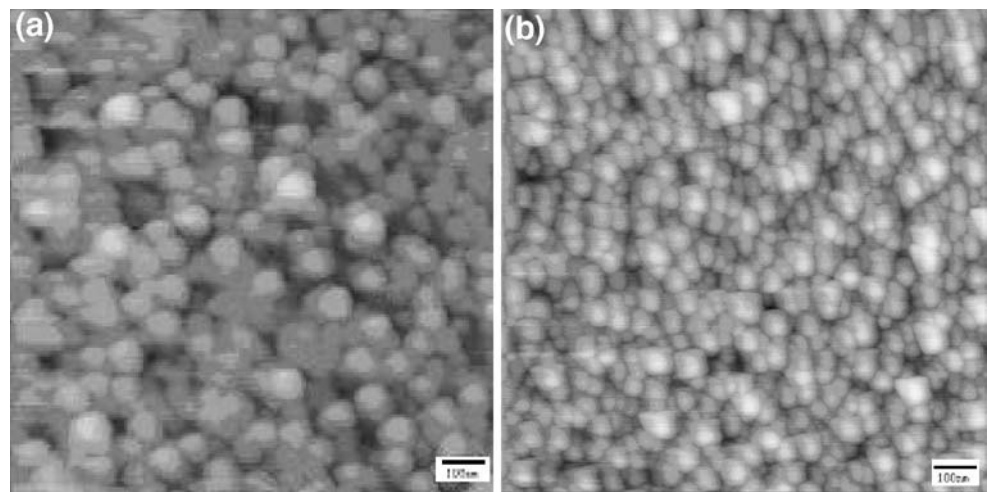
where  $I_{HKL}^*$  and  $I_{H'K'L'}^*$  stands for the XRD peak intensity in BST powder,  $I_{HKL}$  and  $I_{H'K'L'}$  stand for the XRD peak intensity in BST thin films,  $N$  stands for the number of peaks observed in the XRD pattern.

The calculated TC value were 40% (for BST/LNO/Si), 48.1% (for BST/LNO/SiO<sub>2</sub>), and 40% (for BST/LNO/Pt) for type 2 thin films. For comparison, the TC value of type 1 thin films were also calculated: 26.9% (for BST/Si),

**Fig. 2** FESEM pictures of BST thin films on Pt substrate without (a) and with (b) LNO layer



**Fig. 3** AFM micrographs of BST thin films on Pt/Ti/SiO<sub>2</sub>/Si substrate without (a) and with (b) LNO interlayer



23.7% (for BST/SiO<sub>2</sub>), and 23.9% (for BST/Pt). It is clear that type 2 thin films have a (100) TC value as large as twice of type 1 thin films. Only the BST thin films with LNO layer have the special preferential orientation, and their TC values are almost the same, so it is concluded that the different substrates influence the preferential orientation slightly, and the strong influence on the preferential orientation is the LNO interlayer.

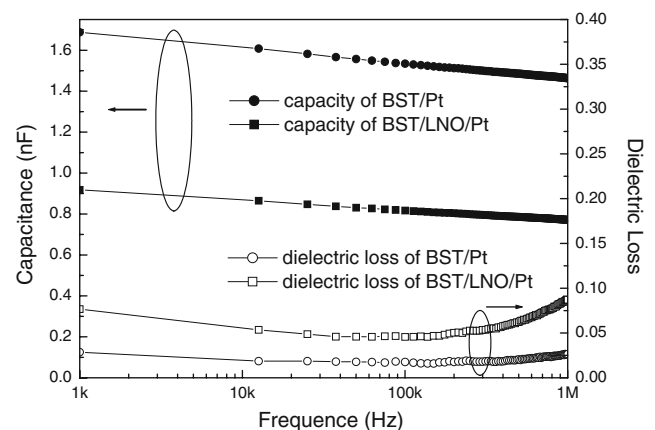
We would like to explain this preferential orientation phenomenon as follows: LNO has the same perovskite structure as BST, so LNO can serve as the seeding layer to decrease the active energy for the crystallization of the perovskite BST thin film; it is easier for BST to crystallize on it at a lower temperature. Stress will form between the crystallized BST and the LNO. This stress, which grows during the annealing process as a result of the different thermal expansion coefficient between BST and LNO, makes the BST grow with a preferential orientation. The amorphous area in the not perfectly crystallized LNO reduced or released the stress, thus the BST thin films are not fully oriented. As to some reports, the BST thin film always form perfect (100) preferential orientation on LNO (100) single crystal substrate, in which stress is formed throughout the whole interface between the LNO(100) and BST thin film, thus the preferential orientation is improved [7, 11].

BST thin films deposited directly on the substrate show different crystallization behavior. It is difficult for nucleation to occur in the film/substrate interface; as a result, homogeneous nucleation may only occur in the bulk of the film, thus the crystallization process may be slower, and the interface stress would be weaker or sometimes will be very small. In this case, the films may grow with less preferential orientation or no orientation as shown in the XRD patterns [12].

The different surface structure of the BST thin films deposited on LNO/Pt and Pt were characterized by FESEM and were shown in Fig. 2. It is observed that BST/Pt is

crack-free and void-free with uniform distributed grains, whereas BST/LNO/Pt possesses irregular grains. The average grain size calculated from the FESEM picture are 90 and 50 nm for BST/Pt and BST/LNO/Pt, respectively. The different surface roughness of BST/LNO and BST/Pt was examined by AFM and were shown in Fig. 3. It was found that the typical average roughness (RMS) values were 2.13 and 10.28 nm for BST/LNO and BST/Pt, respectively. We can interpret the different surface roughness values as follows: first, the surface roughness of LNO layer is much less than Pt; second, the grains of BST thin film on LNO are much smaller.

Figure 4 presents the dielectric properties of thin films on Pt substrate. It is found that BST thin films on Pt have lower dielectric loss and larger capacitance. Considering the thin films were deposited with the same layers by the same process, they should have the same film thickness, so the BST/LNO/Pt thin film has larger dielectric constant. It is because the dielectric properties of ferroelectric thin film is strongly affected by the grain size. The larger grain size of BST/Pt thin film results in larger polarization and,



**Fig. 4** Capacitance and dielectric loss as a function of applied frequency for BST/Pt and BST/LNO/Pt

therefore, a higher value of dielectric capacitance and a lower dielectric loss [13].

#### 4 Conclusion

BST thin films were deposited on different substrates with or without LNO interlayer. XRD examination found that the BST thin films deposited with a LNO interlayer have (100) preferential orientation, the TC is as twice as the thin films deposited directly on the substrate. FESEM observations showed the thin films deposited on LNO/Pt and Pt have grain size about 50 and 90 nm, respectively. The preferential orientation phenomenon is found to be induced by the micro-strain, which rises from the interface of the BST thin film and the LNO interlayer. Dielectric property measurement found BST thin films with LNO interlayer have lower capacitance and bigger dielectric loss, which is caused by its smaller grains.

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