

Structure and dielectric properties of $\text{Ba}(\text{Sn}_{0.2}\text{Ti}_{0.8})\text{O}_3$ thin films grown on different substrates by a sol-gel process

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Abstract $\text{Ba}(\text{Sn}_{0.2}\text{Ti}_{0.8})\text{O}_3$ (BTS) thin films were deposited on Pt/Ti/SiO₂/Si and LaNiO₃/Pt/Ti/SiO₂/Si substrates by a sol-gel processing technique, respectively. The influences of substrates on the phase and microstructure of the thin films were examined. Dielectric properties of the thin films were investigated as a function of frequency and direct current electric field. The results showed that the substrates strongly influenced the microstructure and the dielectric properties of the films. The properties of BTS thin films on LaNiO₃/Pt/Ti/SiO₂/Si substrates were superior to that of the films grown on Pt/Ti/SiO₂/Si substrates.

Keywords Thin films · Sol-gel · Substrate · Microstructure · Tunability

1 Introduction

Ferroelectric thin films have been studied extensively due to their various interesting properties and applications, such as ferroelectric memories, tunable microwave devices, infrared sensors, etc [1, 2]. Among them, a large number of lead-free BaTiO₃-based thin films exhibit a relaxor behavior whose characteristics were related to the type of ionic substitution and to the substitution rate. Some of these materials could prove valuable because they are environment-friendly. Barium tin titanate $\text{Ba}(\text{Sn}_x\text{Ti}_{1-x})\text{O}_3$ (BTS) is a solid solution compound that exhibits paraelectric or ferroelectric proper-

ties depending on the specific composition and temperature [3]. The dielectric constant of BTS can also be controlled electrically by applying a direct current (DC) electric field bias across it. Field dependent dielectric constant of BTS may be exploited for radio frequency (RF) and microwave tunable filter applications [4, 5].

There are various methods for changing the properties of the ferroelectric films, such as the control of heat treatment condition, the insertion of a seed layer and/or different bottom electrodes [6–8]. The LaNiO₃ (LNO) electrode has been used as an oxide electrode with low lattice mismatch to many perovskite ferroelectric materials. The similarities in crystal structural and lattice constants between the electrodes and BTS films offer the benefits of better lattice matching and structural compatibility, and the potential for improved dielectric properties.

In this work, $\text{BaSn}_{0.2}\text{Ti}_{0.8}\text{O}_3$ thin films were deposited on the Pt/Ti/SiO₂/Si and LNO/Pt/Ti/SiO₂/Si substrates by sol-gel technique, respectively. We studied the effect of substrates on the orientation and electrical properties of the BTS thin films. The influence of the concentration of the spin-on solution on crystalline microstructure and electrical properties of the films was also investigated.

2 Experimental

Barium acetate [$\text{Ba}(\text{CH}_3\text{COO})_2$], dibutyltin oxide [$(\text{C}_4\text{H}_9)_2\text{SnO}$], and tetra-n-butyl titanate [$\text{Ti}(\text{OC}_4\text{H}_9)_4$] were used as starting materials. Glacial acetic acid (CH_3COOH), 2-methoxyethanol ($\text{CH}_3\text{OCH}_2\text{CH}_2\text{OH}$), and ethylene glycol ($\text{CH}_2\text{OHCH}_2\text{OH}$) were used as solvent and polymerizing agents, respectively. Barium acetate and dibutyltin oxide were mixed according to a predetermined ratio and then added in the glacial acetic acid solution and heated to 120°C to reflux

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1 h. The ratio (Ba+Sn): glacial acetic acid was equal to 1:10 mol. After cooling to room temperature, the solution was mixed with the solution of tetra-*n*-butyl titanate and acetylacetonone (AcAc $\text{CH}_3\text{COCH}_2\text{COCH}_3$; Ti:AcAc=1:2 mol) under continuous stirring. Finally, 2-methoxyethanol and ethylene glycol were added to control viscosity, cracking of films and the concentration of solution. The concentration of the final solution was adjusted to about 0.1 and 0.3 M, respectively. After aging the precursor solution for 24 h, the spin-coating technique was employed to deposit the gel film on the Pt/Ti/SiO₂/Si (100) and LNO/Pt/Ti/SiO₂/Si (100) substrates by spin coating at 3,000 rpm for 20 s each layer, respectively. Each spin-coated BTS layer was subsequently heat-treated in air at 500°C on a hot plate for 15 min. The coating and heat treatment procedures were repeated until reaching the desired thickness. Finally, the samples were heated at 700°C for 30 min to crystallize the amorphous films. BTS films with a thickness of 270 nm (0.1 M spin-on solution) and 360 nm (0.3 M spin-on solution) were grown in this study.

The crystalline phase of the thin films was identified by X-ray diffraction (BRUKER D8 Advance diffractometer). The film thickness and the surface morphology were determined by FESEM (FEI Quanta 200 FEG). For the electrical measurement, gold electrode pads of 500 μm square were made on top of the BTS thin films by DC-sputtering. The current–voltage (*I*–*V*) characteristics were measured using a Keithley 6517A.

The capacitance–voltage (*C*–*V*) and capacitance–frequency (*C*–*f*) characteristics were measured using an Agilent 4284A LCR meter.

3 Results and discussion

The X-ray diffraction patterns of the BTS thin films deposited on different substrates annealed at 700°C are shown in Fig. 1. It is evident that all films exhibit a single perovskite phase.

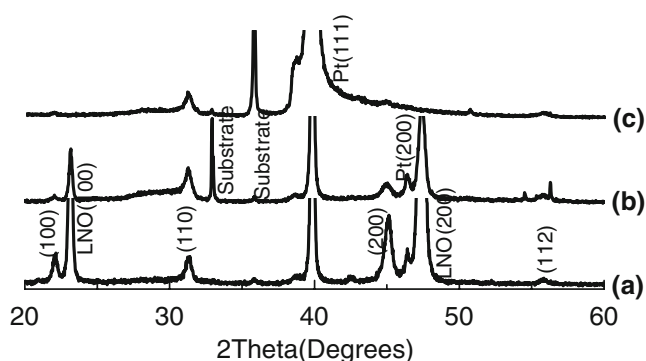


Fig. 1 XRD patterns of BTS thin films with different substrates and precursor concentration: (a) BTS/LNO/Pt/Ti/SiO₂/Si, 0.1 M (b) BTS/LNO/Pt/Ti/SiO₂/Si, 0.3 M (c) BTS/Pt/Ti/SiO₂/Si, 0.1 M

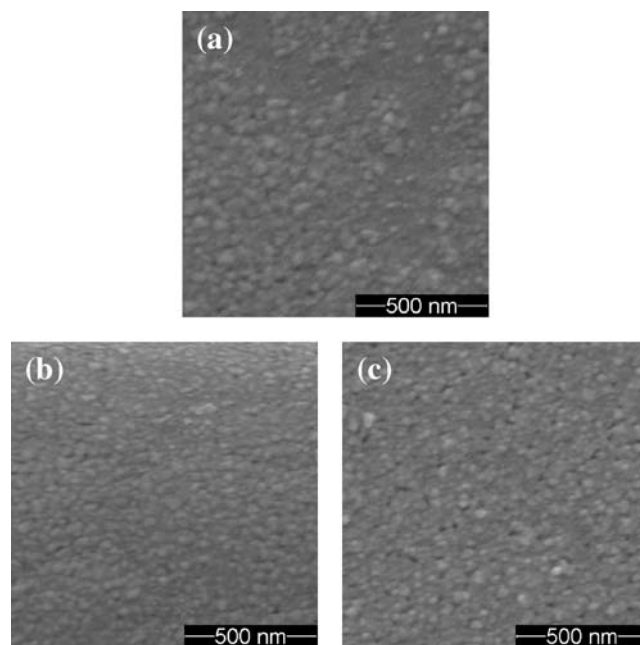


Fig. 2 The FESEM images of BTS thin films with different substrates and precursor concentration: (a) BTS/Pt/Ti/SiO₂/Si, 0.1 M (b) BTS/LNO/Pt/Ti/SiO₂/Si, 0.1 M (c) BTS/LNO/Pt/Ti/SiO₂/Si, 0.3 M

The BTS thin films deposited on LNO substrates showed a (100) preferred orientation while those deposited on Pt substrates had no (100) preferred orientation. This result shows that the use of LNO buffer layer provides an excellent template facilitating the grain-on-grain growth so that highly oriented thin films with much improved properties are realized. Figure 1(b) shows the BTS thin film deposited on LNO substrates with 0.3 M concentration solution. No obviously (100) preferred orientation was observed. It is envisaged that for sufficiently dilute spin-on solution, the single-coated layer is very thin (~14 nm for 0.1 M) and the condensation rate is low, therefore local grain-on-grain growth, or homoepitaxy, would occur at the interface between the new and the previous coating layer, thus resulting in highly preferred orientation [9]. On the other hand, when the spin-on solution concentration increases, each spin-on layer becomes thicker (~45 nm for 0.3 M) because of the more abundant supply of molecules. Consequently, random nucleation would occur, giving rise to polycrystalline orientation [10, 11]. This result shows that the concentration of the precursor solution has a strong influence on the structure and orientation of the BTS thin films deposited on LNO substrates.

Figure 2 shows the surface morphologies of the BTS thin films deposited on different substrates. It can be clearly seen that the BTS thin films deposited on LNO substrates had more uniform grain size and smoother surface than the film on Pt substrates. This result suggests that the substrates substantially influence the crystallization behavior and the

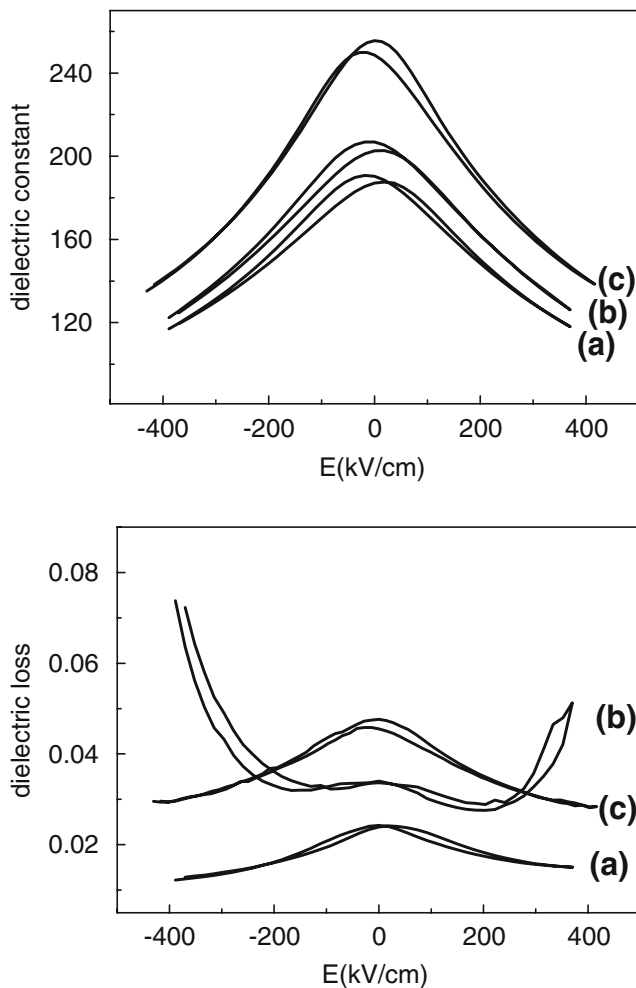


Fig. 3 Dielectric constant and dielectric loss versus DC field for BST thin films with different substrates and precursor concentration (measured at 100 KHz): (a) BTS/Pt/Ti/SiO₂/Si, 0.1 M (b) BTS/LNO/Pt/Ti/SiO₂/Si, 0.1 M (c) BTS/LNO/Pt/Ti/SiO₂/Si, 0.3 M

microstructure of BTS thin films. Figure 2(c) shows the FESEM image of the BTS thin film deposited on LNO substrates with 0.3 M solution. It can be seen that the films deposited with dilute precursor solution (0.1 M) had denser microstructure. This behavior suggests that the concentration of precursor solution substantially influences the crystallization behavior and the microstructure of BTS thin films on LNO substrates.

The dielectric properties of the BTS thin films in Au/BTS/Pt and Au/BTS/LNO configurations were measured at room temperature as a function of the applied voltage. Figure 3 shows the evolution of the dielectric constant and dielectric loss of the BTS thin films deposited on different substrates (measured at 100 KHz). The dielectric constant of the BTS thin films deposited on LNO substrates was relatively higher than those of BTS thin films grown on Pt substrates. This enhancement of dielectric constant was attributed to the orientation and the lattice-matched crystal-

lization of the BTS thin films on LNO substrates [12]. The loss tangent characteristic are different in the positive and negative voltage region, especially for the thin film deposited on the LNO substrates with 0.1 M solution. The asymmetry in the $\tan \delta - E$ characteristic is due to the defects (vacancy, movable ion, leaky grain boundary, etc) [13]. This phenomenon implies that interfaces cast a larger effect on the asymmetry.

The tunability (k) can be calculated by using the expression as following

$$k = \frac{\varepsilon(0) - \varepsilon(E)}{\varepsilon(0)} \quad (1)$$

where $\varepsilon(0)$ and $\varepsilon(E)$ represent the dielectric constant at zero and a certain E field, respectively. The tunability of the BTS thin films deposited on LNO and Pt substrates was 36.4 and 36.1% at an applied field of 350 kV/cm and measurement frequency of 100 kHz. In general, tunability is roughly proportional to the dielectric constant. A material with higher dielectric constant possesses larger tunability [14].

In addition to the dielectric properties, the leakage current characteristics of BTS thin film are also very important properties because they are closely related to the reliability of the device. Figure 4 shows the leakage current characteristics of the BTS thin films on different substrates measured at room temperature. It can be seen that the leakage current density of the BTS thin films deposited on LNO substrates was $5.56 \times 10^{-8} \text{ A/cm}^2$, which was lower than those of the BTS thin films deposited on Pt substrates ($2.46 \times 10^{-5} \text{ A/cm}^2$) when the applied electric field reached 200 kV/cm. This behavior is due to that the more uniform grain size and smoother surface (showed in Fig. 2). The leakage current density of the BTS thin films deposited with 0.3 M spin-on solution on LNO substrates was also showed in Fig. 4 [curve (c)]. It was about three orders of magnitude higher than that of

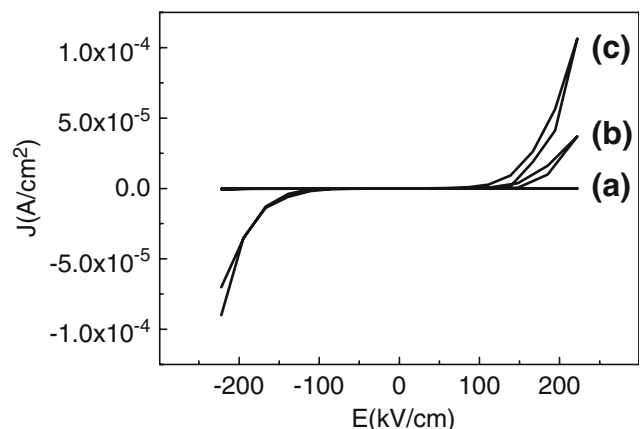


Fig. 4 J–V characteristics of BTS thin films with different substrates and precursor concentration: (a) BTS/LNO/Pt/Ti/SiO₂/Si, 0.1 M (b) BTS/Pt/Ti/SiO₂/Si, 0.1 M (c) BTS/LNO/Pt/Ti/SiO₂/Si, 0.3 M

0.1 M spin-on solution deposited films at 200 kV/cm. This behavior is attributed to the denser microstructure (showed in Fig. 2) of the BTS thin films deposited with dilute precursor solution (0.1 M). The leakage current characteristics are distinctly different in the range of higher dc fields, both in the positive and negative voltage region. This may be caused by generation of a different amount of oxygen vacancy at the top Au/BTS interface and at the bottom Pt/BTS interface [15]. The asymmetry between the positive and negative voltage parts of the J - V characteristic could be attributed to oxygen vacancies and movable ions at the top Au/BTS interface and the bottom LNO/BTS interface [15, 16], which is consistent with the C - V results.

4 Conclusions

Ba(Sn_{0.2}Ti_{0.8})O₃ (BTS) thin films were deposited on Pt/Ti/SiO₂/Si and LaNiO₃/Pt/Ti/SiO₂/Si substrates by a sol-gel processing technique, respectively. This investigation demonstrated: (1) The crystallization ability and electrical properties of the BTS thin film depended on the substrates. The BTS thin films deposited on LNO/Pt/Ti/SiO₂/Si substrates showed more uniform grain size, smoother surface, higher dielectric constant and tunability, and lower leakage current density than the BTS thin films deposited on Pt/Ti/SiO₂/Si substrates. (2) The concentration of precursor solution can strongly influence the orientation and microstructure of BTS thin films on LNO/Pt/Ti/SiO₂/Si substrates. The BTS thin films deposited with dilute precursor solution (0.1 M) showed a (100) preferred orientation and denser microstructure than the films deposited with higher precursor solution (0.3 M).

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