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Ferroelectric properties of $Ba_{1-x}Sr_xTiO_3$ thin films synthesized by using novel sol–gel technique through carbonates

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Abstract $Ba_{1-x}Sr_xTiO_3$ (BST) thin films were prepared on the substrate of $Pt/Ti/SiO_2/Si$ by using novel sol–gel process through carbonates. The surface morphology and domain contrast of the films were investigated by atomic force microscopy (AFM), and the domain structures of the BST film were observed when AFM were operated in piezoelectric force microscopic (PFM) analysis and in the friction mode (FFM). The ferroelectric properties of the films were also investigated. It is shown that BST films obtained by the new sol–gel process through carbonates exhibit good properties.

Keywords BST thin films · Sol–gel · Carbonates · Domain structure · Ferroelectricity

1 Introduction

Barium strontium titanate, $Ba_{1-x}Sr_xTiO_3$ (BST), is a continuous solid solution of ferroelectric $BaTiO_3$ and paraelectric $SrTiO_3$, and its properties can be tailored by changing the composition according to the requirement of the electronic device under consideration. The properties of BST thin films, along with the high dielectric constant, low dielectric loss, no polarization fatigue, and composition-dependent Curie temperature [1–3], make the material attractive candidate for microelectronic devices.

In the preparation of these materials, sol–gel methods have been extensively employed because of the advantages like, easier composition control, better homogeneity, low processing temperature, fabrication of large area thin films and low equipment cost. Among the reported sol–gel processes to fabricate the BST thin films, various metal–organic compounds were adopted as Ba, Sr and Ti sources. The precursor compounds can be mainly divided into two classes: the metal alkoxides and carboxylates. Barium strontium carboxylates were usually employed as corresponding metal sources instead of barium strontium alkoxides because the alkoxides are very easy to hydrolyze and difficult to control during the processing. Barium carbonate and strontium carbonate are basic starting chemical materials, the acetates or alkoxides of Ba & Sr, which are not easily obtained or very expensive, are always fabricated from their carbonates in industry.

In this work, the preparation of $Ba_{1-x}Sr_xTiO_3$ (BST) thin films by using novel sol–gel process through carbonates, the domain contrast and the ferroelectric properties of BST thin films prepared were investigated.

2 Experimental

Barium carbonate, strontium carbonate and titanium-tetrabutoxide were used as starting materials. Glacial acetic acid and 2-methoxyethanol were used as the solvents. In order to prepare $Ba_{0.8}Sr_{0.2}TiO_3$ thin films, initially barium acetate and strontium acetate were taken in the ratio of 80:20 and dissolved in the mixture of acetic acid and 2-methoxyethanol at 120 °C for 3 h to obtain clear solution. Titanium-tetrabutoxide was dissolved in 2-methoxyethanol mixing with acetic acid to form chelate complex. The dissolved barium and strontium precursor solution was dropped into titanium-tetrabutoxide precursor solution to get sol. The final sol with the concentration of 0.3 mol/l was then achieved by adding 2-methoxyethanol, which also improved the wet-stability and uniformity of films derived.

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Pt/Ti/SiO2/Si substrates were used for the deposition of BST films in present study. The precursor solution was coated on the substrates by spin coating at a rate of 5,000 rpm for 20 s. After coating, films were heating at 450 °C for 5 min in order that the residual organics can be pyrolyzed, and this process was repeated for several times to get the needed film thickness. A heat-treatment of films was followed at 650, 700, 750 and 800 °C for 30 min in air, respectively. And the films were cooled to room temperature slowly. The crystallographic structure of the films obtained was investigated by X-ray diffraction as reported in former paper [4], showing that the films possess pure perovskite structure.

For electronic measurement, Au top electrode with a diameter of 2 mm was deposited by DC-sputtering through a designed mask onto the film surface, and the bottom electrode was the Pt/Ti/SiO2/Si substrate.

3 Results and discussion

3.1 Surface roughness and morphology

In order to characterize the surface roughness and morphology of the films and to investigate the domain contrast in scanning probe microscopy (SPM), the samples were measured in an ambient environment by means of a commercially available microscope (SPA-300HV, Seiko Instruments, operating both in PFM and FFM modes). Figures 1(a) and 2(a) show the AFM micrographs of the surface of BST film annealed at 750 °C for 30 min. It can be seen from Figs. 1(a) and 2(a) that the film was very dense, smooth and crack free, and the average grain size was approximately 70 nm. The surface roughness was 3.5 nm.

3.2 Domain analysis

The measurement principles of local ferroelectricity can be found in the literature [5–7]. The present setup makes it possible to measure the local ferroelectricity of the films in situ by switching to the respective modes. Therefore, surface morphology and ferroelectric images can be obtained on the same sample region. The piezoelectric force microscopic (PFM) analysis was used to characterize piezoelectric properties of the surface. PFM vertical (v-PFM) surface displacement is induced by tip bias. Vertical components of signal are related to in-plane and out-of-plane polarization components.

Figure 1 illustrates the simultaneous topographic and piezo-response images of the films at a constant tip-sample bias of 5 V in PFM mode. In Fig. 1(b), the brighter the area, the larger ferroelectric domain directed out of the surface; the darker the area, the larger ferroelectric domain directed in the surface. It also can be seen that some domain's contrast is simple bright in a grain (for example, the one marked grain 1), some domain's contrast is simple dark in a grain (for example, the one marked grain 2), and some opposition domain's contrast is both bright and dark in same grain (for example, the one marked grain 3).

The AFM was also operated in friction mode to characterize piezoelectric properties of the thin film. The origin of domain contrast observed in the friction mode can be explained by the difference in lateral forces acting on the AFM tip from the domains with different direction of spontaneous polarization This mechanism of domain contrast becomes significant during acquisition of the image when the tip is scanning perpendicular to the length axis of the cantilever [8]. Figure 2 illustrates the simultaneous topographic image and effect of polarization charge

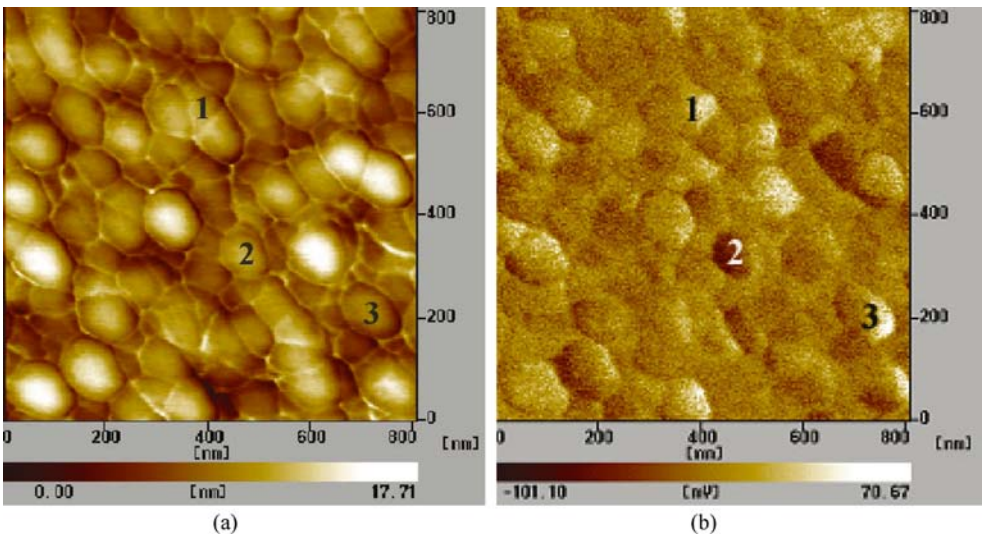

Fig. 1 Simultaneous topographic (**a**) and piezo-response (**b**) images of the films at a constant tip-sample bias of 5 V in PFM mode

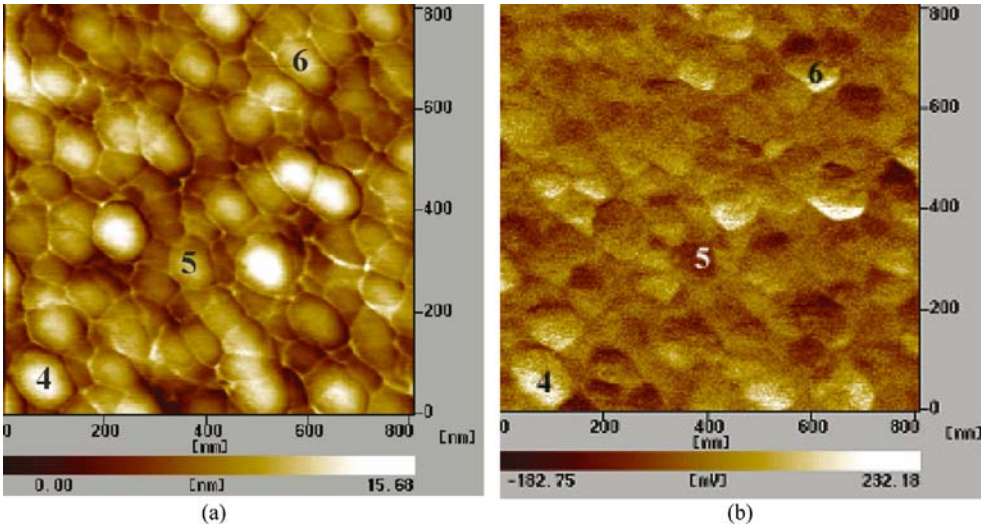

Fig. 2 Simultaneous topographic (**a**) and domain patterns (**b**) images of the films at a constant tip-sample bias of 5 V in FFM mode

on surface friction. In Fig. 2(b), the brighter the area, the larger ferroelectric domain directed one orientation of the surface; the darker the area, the larger ferroelectric domain directed the opposition in the surface. It also can be seen that, some domain's contrast is simple bright in a grain (for example, the one marked grain 4), some domain contrast is simple dark in a grain (for example, the one marked grain 5), and some opposition domain's contrast is both bright and dark in same grain (for example, the one marked grain 6).

3.3 Dielectric property and capacitance–voltage characteristics

The dielectric and ferroelectric behaviors of the BST thin films were measured in the metal-BST-metal configuration with the films sandwiched between the bottom platinum and top gold electrodes. The capacitance value at different spots of the film varied within less than 3%, indicating a good homogeneity in thickness of the film prepared by spin-coating techniques. The dielectric constant at frequency of 100 kHz was 564 (Fig. 3). The dielectric constant for BST thin film was much higher than that reported by Tahan et al. [1] for films deposited by the sol–gel technique on Pt/Si substrate with same composition and thickness 400 nm, which showed a lower dielectric constant 400 at 1 kHz. One of the reasons may be the effect of process techniques on the dielectric properties of BST thin film. It is clear that the dielectric constant decreases with the increasing of the frequency. When the frequency is higher than 200 kHz the dielectric constant of the film is almost near to 100.

The bias voltage dependence of the capacitance was studied in the thick film, derived by using the same technique, of about 2 μm measured through the cross-view of SEM image. Figure 4 shows the capacitance–voltage (*C–V*) characteristic of the BST thin film. The dependence of the capacitance as a function of the voltage shows a strongly non-linear character, and two peaks characterizing spontaneous polarization switching can be clearly seen in the figure indicating that the films have a ferroelectric nature. Usually, *C–V* curves of ferroelectric BST films are butterfly-shaped with two maxima of capacitance close to

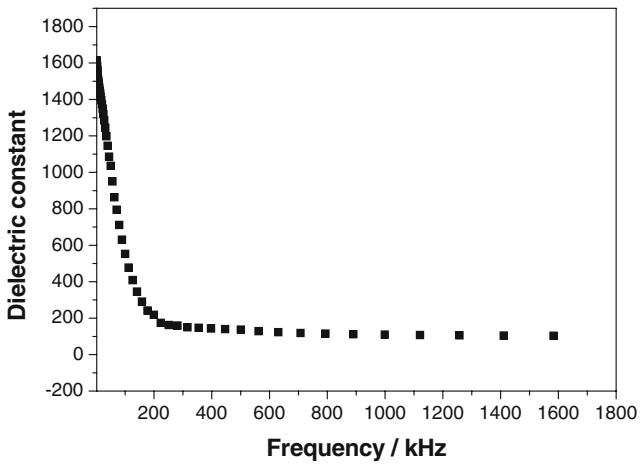

Fig. 3 Dielectric constant of BST thin films as a function of frequency

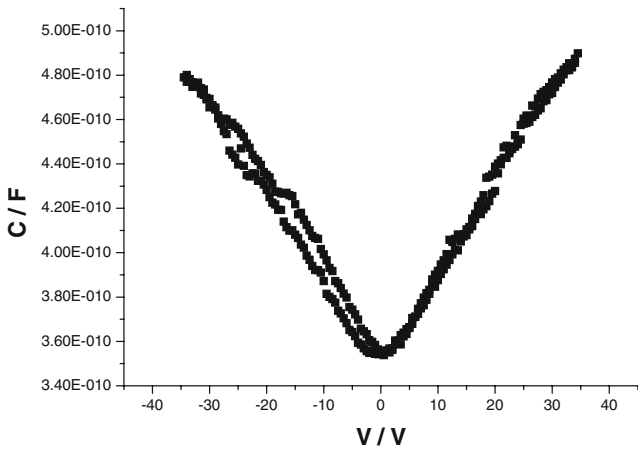

Fig. 4 *C–V* curves of thin films at the frequency of 100 kHz

0 V. In the operating conditions, the film's butterfly-shaped *C–V* curve was not fully observed because the applied voltage of the instrument is limited for the measured film. That is to say the curve of Fig. 4 is a mediacy of the *C–V* characteristic of the BST thin film.

4 Conclusion

Barium strontium titanate thin films with ferroelectric characteristics, deposited on a platinum-coated silicon substrate by the spin-coating techniques, were successfully obtained using the carbonate precursor method, producing polycrystalline BST thin films with tetragonal perovskite structure. Dense, homogenous, crack-free and smooth BST thin films with uniform thickness and uniform grain size were produced by spin-coating techniques and thermal annealing in a conventional furnace at 750 °C. The domain contrast of the film is observed both in PFM and FFM, the results indicate the films have ferroelectric properties. The electrical characteristics of the thin films showed good dielectric and ferroelectric properties.

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