Thickness dependence of in-plane dielectric and ferroelectric properties of $Ba_{0.7}Sr_{0.3}TiO_3$ thin films epitaxially grown on $LaAlO_3$

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The authors have studied the effects of film thickness on the lattice strain and in-plane dielectric and ferroelectric properties of $Ba_{0.7}Sr_{0.3}TiO_3$ thin films epitaxially grown on $LaAlO_3$ (001) single crystal substrates. With increasing film thickness from 20 to 300 nm, the in-plane lattice parameter (a) increased from 0.395 to 0.402 nm while the out-of-plane lattice parameter (c) remained almost unchanged, which led to an increased a/c ratio (tetragonality) changing from 0.998 to 1.012 and consequently resulted in a shift of Curie temperature from 306 to 360 K associated with an increase of the in-plane remnant polarization and dielectric constant of the film. © *2007 American Institute of Physics*. [DOI: 10.1063/1.2716865]

It has been observed that the film thickness of ferroelectric materials has a significant impact on the dielectric and ferroelectric properties of the film due to a number of complex factors, including lattice distortion, defects (point defects, dislocations, etc.), and so-called "dead layers."[1–6] In the literature, the thickness effect has been studied typically by comparing the capacitances of a series of samples having a conventional metal-ferroelectric-metal (MFM) configuration and with a varying thickness of the ferroelectric thin film. By assuming that a nonferroelectric interface (dead layer) exists between the film and the electrode and applying a series-capacitance calculation, the thickness effect—in particular, the thickness dependence of the apparent dielectric constant of the films—could be quantitatively explained. The major limitation of this method is that the influence of the dead layer is so dominant that the influences coming from other factors (such as lattice distortion and defects) in the films cannot be easily extracted from the measurement results, let alone the possible structure and property change along in-plane directions. In order to study the in-plane properties, one may instead use thin films in a coplanar capacitor (with an electrode/ferroelectric film/substrate configuration), in which the dead-layer effect can be neglected and the influences of lattice distortion and defects of the films on the properties can be directly observed.[7,8] As we have noticed, however, the investigation of the thickness effect based on the in-plane dielectric and ferroelectric measurements is rather limited.[9]

In this letter, we report on the study of the thickness dependence of the lattice strain and in-plane dielectric and ferroelectric properties of $Ba_{0.7}Sr_{0.3}TiO_3$ (abbreviated as BST) thin films epitaxially grown on $LaAlO_3$ (LAO) single crystal substrates. BST is an important ferroelectric oxide which has potential applications in tunable microwave components (phase shifters, filters, etc.). In our experiment, $Ba_{0.7}Sr_{0.3}TiO_3$ thin films with thickness (t) ranging from 20 to 300 nm were grown on LAO (001) single crystal substrates by pulsed laser deposition, using a KrF excimer laser (Lambda Physik COMPex 205, Germany) with a wavelength of 248 nm, energy of 250 mJ, and repetition rate of 10 Hz. During the deposition, the substrate temperature was kept at ~750 °C and the oxygen pressure was 27 Pa. The film thickness was controlled by changing the deposition time (from 1.5 to 22.5 min). After deposition, the samples were annealed at 1000 °C in air for 3 h to improve the crystallinity and reduce oxygen vacancies of the films. The freshly prepared samples were observed under an atomic force microscope (Digital Instrument Nanoscope IV). The average grain size was found to be 30–40 nm in diameter and independent of the film thickness. The crystallographic characterizations of the films were performed on an x-ray diffractometer (Bruker AXS/D8 Discover) equipped with Cu $K\alpha$ radiation with a wavelength of $\lambda = 0.154\,08$ nm. The in-plane dielectric constants and ferroelectric hysteresis loops of BST films were measured using Au/BST/LAO interdigital capacitor configurations. Here Au stands for gold interdigital electrode. The details of the fabrication process and geometric size of the interdigital capacitor samples have been described elsewhere. The dielectric and ferroelectric measurements were carried out on an impedance analyzer (HP4194A, Hewlett-Packard) and a ferroelectric analyzer (TF-2000, Aix-ACCT Systems GmbH, Germany) equipped with a high-voltage module, respectively.[10,11]

The X-ray diffraction $\theta-2\theta$ scans revealed that, regardless of film thickness, all BST films were well crystallized and had a pure perovskite phase. The off-axis ϕ scan of the (202) reflection (data not shown) revealed that the films all grew with a "cube-on-cube" epitaxy on the (001) LAO substrate. The out-of-plane lattice parameter (c) and in-plane lattice parameter (a) of BST were determined using the conventional and off-axis $\theta-2\theta$ scan data (the latter were obtained by tilting the samples at an angle of 45°, followed by the calculation using the equation $a = 2/\sqrt{d_{202}^{-2} - d_{002}^{-2}}$, where d_{202} and d_{002} are the lattice spacings of 202 and 002 planes, respectively[12]). Figure 1 shows the thickness dependence of the lattice parameters. The in-plane lattice parameter a ($=b$) shows a trend of increase with the increasing thickness while the out-of-plane lattice parameter c is almost independent of t. From the figure it seems that $t = 150$ nm is a critical

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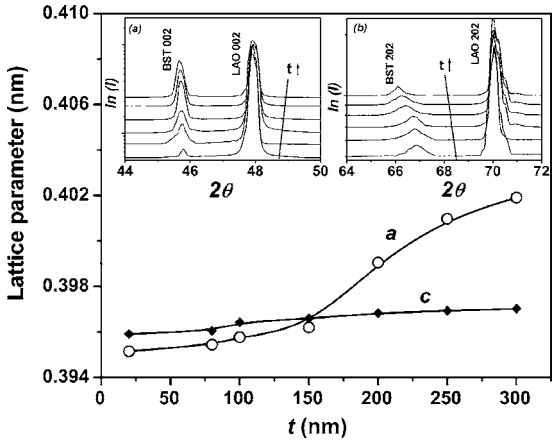

FIG. 1. In-plane (a) and out-of-plane (c) lattice parameters of $Ba_{0.7}Sr_{0.3}TiO_3$ thin films grown on $LaAlO_3$. The inset shows the x-ray diffraction patterns of (a) the conventional $\theta/2\theta$ scan and (b) off-axis $\theta/2\theta$ scan.

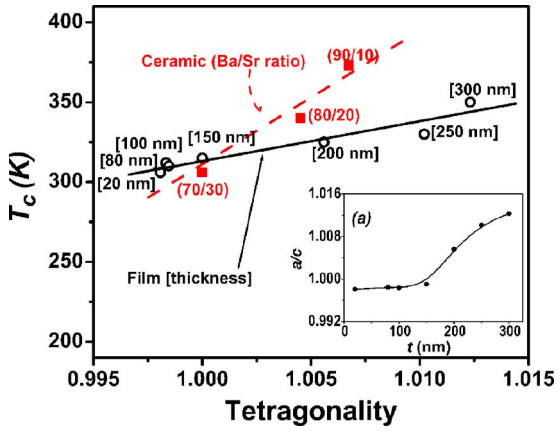

FIG. 3. Curie temperature vs tetragonality in $Ba_{0.7}Sr_{0.3}TiO_3$ thin films grown on $LaAlO_3$ substrate and bulk $Ba_{0.7}Sr_{0.3}TiO_3$ ceramics. The inset shows the thickness dependence of tetragonality of the thin films.

value. (1) BST with $t=150$ nm has a cubic lattice with $a=c=0.3966$ nm, which is the same as that of the $Ba_{0.7}Sr_{0.3}TiO_3$ ceramics ($a=c=0.397$ nm).[13] A very slight lattice distortion exists in BST with $t<150$ nm. (2) BST films with $t>150$ nm have a tetragonal symmetry with $a>c$. When $t=300$ nm, for example, $a=0.402$ and $c=0.397$ nm. The ratio of a/c (defined as tetragonality in this study) increases with increasing thickness.[14] This observation of lattice distortion is consistent with the results reported by Chen *et al.*[6] In a $Ba_{0.50}Sr_{0.50}TiO_3$ (900 nm)/LAO (001) heterostructure, Chen *et al.* observed a lateral lattice expansion ($a=0.401$, $c=0.395$ nm) in the $Ba_{0.50}Sr_{0.50}TiO_3$ film and they attributed the distortion mainly to the anisotropic thermal contraction during cooling.[6] We believe that the mechanism is also applicable for our BST films with relatively large thickness. For those BST with smaller thickness ($t<150$ nm), other factors including lattice mismatch and defects may become influential, which compensates with the lattice expansion and makes the lattices less distorted.[15–19]

Accompanying with the change of lattice structure, the in-plane dielectric and ferroelectric properties of the BST films showed strong thickness dependence. Figure 2 shows the temperature dependence of the dielectric constant for

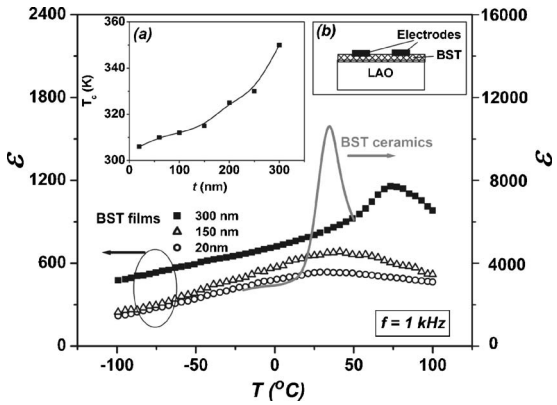

FIG. 2. Temperature dependence of in-plane dielectric constant of $Ba_{0.7}Sr_{0.3}TiO_3$ films on $LaAlO_3$ and dielectric constant of $Ba_{0.7}Sr_{0.3}TiO_3$ ceramics. The inset (a) shows the relationship of the Curie temperature of BST films vs the film thickness and inset (b) shows the schematic structure of the thin film samples.

BST films with thicknesses of 20, 150, and 300 nm, respectively. The dielectric properties of BST ceramics (after Ref. 13) were also plotted in the figure for comparison. It was found that (1) all the BST films exhibit a broad ferroelectric-to-paraelectric phase transition which can be explained as the result of nanoscaled grain sizes of the films. (2) The Curie temperature (T_C) shifts to high temperatures as the film thickness increases, as shown in Fig. 2(a). For example, when with $t=20$ nm, $T_C\approx296$ K; when $t=150$ nm, $T_C\approx309$; and when $t=300$ nm, $T_C\approx360$ K. (3) The value of dielectric constant of the films increases with increasing film thickness but is always much smaller than that of the ceramics.

We owe the above-mentioned T_C shift to the lattice distortion of BST caused by the lateral expansion. Similar phenomena have been investigated in recent years in typical ferroelectric films such as barium titanate and strontium titanate.[7,8] By choosing appropriate substrates, for example, epitaxial strain can be introduced to the thin film of barium titanate which eventually leads to an increase in T_C by nearly 500 °C.[7] While in our work the dielectric measurement was conducted in the in-plane direction, the measurements in literature were usually taken along the out-of-plane direction. Despite this difference, the underlying mechanisms for both cases are exactly the same. Figure 3 shows the T_C versus tetragonality dependence of our BST films and BST ceramics (data after Ref. 13). Both show an upward shift of T_C as the tetragonality increases. The difference is that the variation of tetragonality in BST films is realized by changing the film thickness [as shown in Fig. 3(a)], while the variation of tetragonality in the ceramics is obtained by the change of the Ba/Sr ratio. Quite interestingly the latter one seems to be able to more effectively affect the T_C.

As mentioned above, the dielectric constant of the BST films increases as the film thickness increases. For example, the room-temperature dielectric constants of the films shown in Fig. 3 are ε (20 nm)=540, ε (150 nm)=660, and ε (300 nm)=820, respectively. Such thickness dependence appears to be analogous to literature reports on metal-ferroelectric-metal capacitors but these two cases are actually based on different mechanisms.[19,20] The thickness effect in the MFM capacitors is explained as a result of interface effect. As the film thickness increases, the influence of the nonferroelectric dead layer becomes less significant, result-

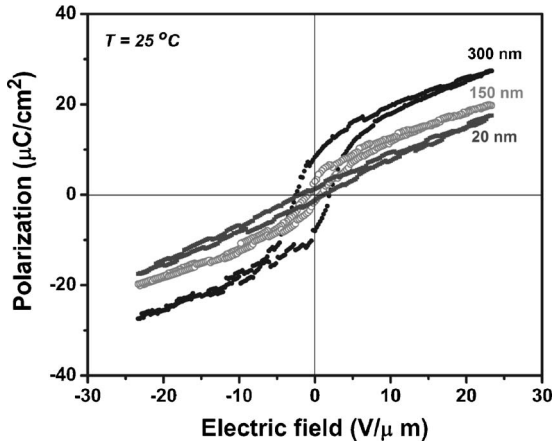

FIG. 4. In-plane ferroelectric hysteresis loop of $Ba_{0.7}Sr_{0.3}TiO_3$ thin films grown on $LaAlO_3$ substrate.

ing in an increase of the effective dielectric constant.[1–6] For our samples, however, the thickness effect cannot be understood by applying such dead-layer model because the capacitance contribution of the dead layer (the interface between the film and the substrate) to the total capacitance of the interdigital capacitor is negligible, according to the partial capacitance model.[21] Instead, the increase of the in-plane dielectric constant with increasing thickness is mainly due to intrinsic enhancement in the ferroelectricity, as we believe.

A trend of enhancement in the in-plane ferroelectric property of the films has been observed. Figure 4 shows hysteresis loops for the films with thicknesses=20, 150, and 300 nm, respectively. Due to different T_C, the three films are in different states (ferroelectric or paraelectric) at room temperature. The 300-nm-thick film is in a ferroelectric state because its T_C is far above room temperature; correspondingly the hysteresis loop of the film is a well-defined (although not fully saturated) ferroelectric loop with a remnant polarization (P_r) of 8.4 $\mu C/cm^2$ and coercive field (E_c) of 2.2 $V/\mu m$. The hysteresis loop of the film with $t=150$ nm is poorly defined (but still indicative of ferroelectric). For the film with $t=20$ nm, the polarization-electric field curve cannot be regarded as a typical ferroelectric one. We believe that the enhanced in-plane ferroelectricity in thicker films is also a result of the increased tetragonality. In other words, the mechanism is the same as that for the enhanced ferroelectric properties in strained barium titanate and strontium titanate thin films reported in literature.[7,8]

In summary, epitaxial $Ba_{0.7}Sr_{0.3}TiO_3$ thin films of various thicknesses ranging from 20 to 300 nm were deposited on $LaAlO_3$ (001) single crystal substrates by pulsed laser deposition. The effects of film thickness on the lattice distortion and in-plane dielectric and ferroelectric properties have been studied. It was found that BST films with thickness <150 nm had a *c*-axis elongated tetragonal symmetry while films with thickness >150 nm had an *a*-axis elongated tetragonal symmetry. The in-plane dielectric constant and ferroelectric polarization were observed to have increased as the thickness of the film increased.

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