

Microstructure and enhanced in-plane ferroelectricity of $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ thin films grown on MgAl_2O_4 (001) single-crystal substrate

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The microstructure and in-plane dielectric and ferroelectric properties of highly oriented $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ (BST) thin film grown on MgAl_2O_4 (001) single-crystal substrate through pulsed laser deposition were investigated. X-ray diffraction measurements indicated that BST had a distorted lattice with a tetragonality $a/c=1.012$. The cross-sectional observation under transmission electron microscope revealed that, while most of BST grains grew epitaxially on MgAl_2O_4 , the film also contained a noticeable amount of misoriented grains and dislocations. The electrical measurements indicated that the film had a shifted Curie temperature ($T_C=78^\circ\text{C}$) and an enhanced in-plane ferroelectricity (remnant polarization $P_r=7.1\text{ }\mu\text{C}/\text{cm}^2$) when compared with BST ceramic ($T_C\approx 33^\circ\text{C}$ and $P_r\approx 0$). © 2006 American Institute of Physics. [DOI: 10.1063/1.2402900]

The substrate effect on the dielectric and ferroelectric properties of perovskite-structured oxide thin films has attracted attention in recent years. Some interesting results have been reported. By choosing appropriate substrates, for example, epitaxial strain can be introduced to the thin film of barium titanate (BaTiO_3) which leads to an increase in Curie temperature (T_C) by nearly 500°C and produces a remnant polarization of at least 250% higher than bulk BaTiO_3 single crystals.¹ Similar enhancement of ferroelectricity has also been realized in the thin films of strontium titanate (SrTiO_3), solid-solution barium strontium titanate ($\text{Ba}_x\text{Sr}_{1-x}\text{TiO}_3$, abbreviated as BST), and lead strontium titanate ($\text{Pb}_x\text{Sr}_{1-x}\text{TiO}_3$).²⁻⁵ In these heterostructures, a small mismatch (usually $<5\%$) in the lattice constant between the substrate and the thin film is critical to the epitaxial growth of the film. The status of the lattice mismatch also has a dominant effect on the direction and quantity of stress in the film. To fulfill these requirements, single crystals with a cubic (or pseudocubic) crystal structure of lattice constants ranging from ~ 0.37 to 0.42 nm such as MgO , LaAlO_3 , LSAT, and SrTiO_3 are often used in the literature.⁶⁻¹⁰

This study aims to examine the microstructure and in-plane dielectric and ferroelectric properties of $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ (BST) thin film grown on MgAl_2O_4 single crystal substrate. $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ has a perovskite structure with a lattice constant $a_{\text{BST}}=0.397\text{ nm}$ at room temperature, while MgAl_2O_4 has a spinel-type structure with a lattice constant of $a_{\text{MgAl}_2\text{O}_4}=0.808\text{ nm}$, about two times of a_{BST} . The small lattice mismatch ($|2a_{\text{BST}}-a_{\text{MgAl}_2\text{O}_4}|/a_{\text{MgAl}_2\text{O}_4}\approx 1.7\%$) makes it possible for BST to grow epitaxially on MgAl_2O_4 . Because of the small dielectric constant, loss tangent, and high irradiation resistance of MgAl_2O_4 , the heterostructure BST/ MgAl_2O_4 may provide an ideal model structure for tunable microwave devices (the typical heterostructures under current investigation for microwave applications include BST/ LaAlO_3 , BST/ MgO , etc.) So far little research has been conducted regarding this heterostructure although the thin

films of a few other perovskite oxides (e.g., superconductors) have been integrated on MgAl_2O_4 or MgAl_2O_4 -buffered silicon.¹¹⁻¹³

In this study, a 200-nm-thick $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ thin film was deposited on an MgAl_2O_4 (001) single-crystal substrate through pulsed laser deposition using a 248 nm krypton fluoride (KrF) excimer laser (Lambda Physik COMPEX 205). The energy level and repetition rate of the laser were 250 mJ and 10 Hz, respectively. The distance between the target ($\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ ceramic) and the substrate was fixed at 5 cm. During the deposition, the substrate temperature was maintained at 750°C and the oxygen partial pressure was kept at 27 Pa. After deposition, the thin film was annealed in air at 1000°C for 3 h to improve its crystallinity and to reduce oxygen vacancies.

The crystallographic characterization was performed on a Bruker AXS D8 Discover x-ray diffractometer. The surface morphology of the BST thin films was observed using an atomic force microscope (AFM) (Digital Instrument Nanoscope IV) in tapping mode. Transmission electron microscopy (TEM) studies were carried out on a JEOL JEM-2011 microscope operated at 200 kV to observe the crystal structure and interfaces at the atomic level. The sample for the dielectric and ferroelectric measurements had a configuration of coplanar interdigital capacitor. The preparation and sizes of the top interdigital electrodes have been described elsewhere.¹⁴ The ferroelectric hysteresis loop was measured along the in-plane (100) direction on a ferroelectric tester (TF Analyzer 2000, aixACCT) while the in-plane dielectric constant of BST was measured with an HP 4294A impedance analyzer connected to an Oxford temperature controlled chamber.

Figure 1 shows the x-ray diffraction (XRD) results. The $\theta/2\theta$ scan indicates that the BST thin film has a pure perovskite phase with lattices highly oriented along the (001) direction. The rocking curve taken around the BST (002) reflection has a full width at half maximum of $\sim 0.1^\circ$, indicating the good crystallinity of the film. The off-axis ϕ scans of the BST (202) and MgAl_2O_4 (404) reflections reveal a “cube-on-cube” epitaxial growth mode of BST on the spi-

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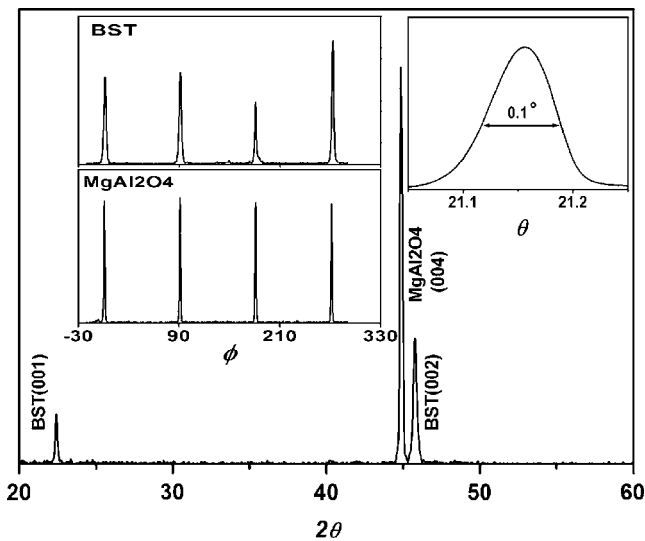


FIG. 1. XRD patterns of $\theta/2\theta$ scan of the heterostructure $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3/\text{MgAl}_2\text{O}_4$. The insets show the rocking curve of the (200) peak (right) and ϕ scan of (202) reflections of the $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ thin film and MgAl_2O_4 substrate (left).

nel. From the XRD patterns, the lattice spacing d_{002} and d_{202} were calculated by using Bragg's equation, and then the out-of-plane lattice parameter c ($=2d_{002}$) and the in-plane lattice parameter a ($=2/\sqrt{d_{202}^2 - d_{002}^2}$) were obtained.¹⁵ It was found that, unlike $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ ceramic which has a cubic lattice structure with $a=c=0.397$ nm, the thin film had a tetragonal lattice with $a=0.3989$ nm, $c=0.3943$ nm, and thus a tetragonality $a/c=1.012$. The expansion of the lattice along the in-plane direction was caused by the lattice mismatch between BST and the substrate. Since MgAl_2O_4 has a spinel-type face-centered-cubic structure with lattice parameters $a=c=0.808$ nm, the lattice parameter of the oxygen sublattice is about 0.404 nm which is $\sim 1.7\%$ larger than BST. The lattice distortion of BST thin film on MgAl_2O_4 is similar to the case of BST on MgO (cubic, $a=c=0.420$ nm). Other factors such as anisotropic thermal contraction and oxygen deficiency may also influence the lattice distortion of BST.^{7,16} The surface morphology of the freshly deposited BST thin film was observed under an atomic force microscope (Digital Instrument Nanoscope IV) in tapping mode (images not shown here). The average grain size was estimated to be about 50 nm in diameter and the root-mean-square roughness was about 2.3 nm over a $1 \times 1 \mu\text{m}^2$ area, implying a flat film surface.

The cross-sectional TEM image taken along [001] zone axis of MgAl_2O_4 in Fig. 2 shows that the BST film has grown columnar and is about 200 nm thick. The density of dislocations is very high near the interface and is reduced as the film becomes thicker. The inset (a) shows the selected area diffraction pattern (SAD) taken in an area including both the substrate and film. Indices are first made for the substrate followed by the film (using italic numbers) when the spots arise simultaneously from the substrate and the film. It should be noted that MgAl_2O_4 belongs to the spinel structure which has a diamond-type structure belonging to fcc unit cell. The 200 diffraction from MgAl_2O_4 is due to multiple scattering even though it is kinematical forbidden. The diffraction pattern demonstrates an epitaxial relationship of (100) BST \parallel (100) MgAl_2O_4 and [010] BST \parallel [010] MgAl_2O_4 between the substrate and the film. However, the

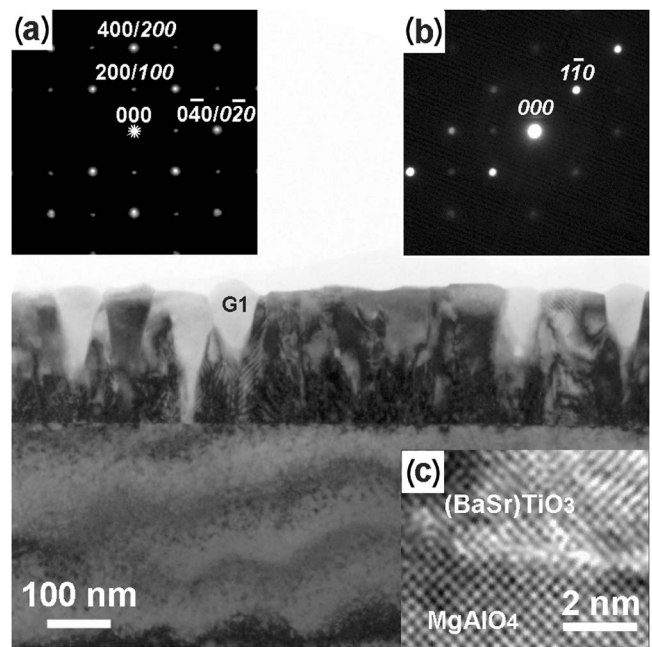


FIG. 2. Cross-sectional structure of $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3/\text{MgAl}_2\text{O}_4$ under TEM. The insets are (a) selected area diffraction pattern (SAD) taken from an interface, (b) NBED diffraction pattern taken at G1, and (c) a high-resolution (600 000) interface image taken at the interface between a well aligned grain and the substrate.

film also contains a noticeable amount of misoriented grains which shows a slight contrast in Fig. 2. Most of these misoriented grains nucleated at the middle of the film which could be caused by the defects generated during the grain growth. The results of the nanobeam electron diffraction (NBED) studies show that the angles of misalignment are various and often exceed 10° . The NBED diffraction pattern in the inset (b) was taken from the grain marked as G1 which shows a tilting of nearly 10° away from the [001] zone axis. Inset (c) is a high resolution image taken at the interface between a well aligned grain and the substrate. It should be noted that the noise of the image has been suppressed by applying a circular mask on the power spectrum of the image. The high resolution image shows the grain has grown epitaxially on the substrate.

The in-plane ferroelectric properties of the BST thin film were determined. Well-defined ferroelectric hysteresis loops were obtained and a typical sample is shown in Fig. 3. Under an external electrical field up to $20 \text{ V}/\mu\text{m}$, the remnant polarization P_r and coercive field E_c of BST were found to be $7.1 \mu\text{C}/\text{cm}^2$ and $1.2 \text{ V}/\mu\text{m}$, respectively. In comparison with $\text{Ba}_{0.70}\text{Sr}_{0.30}\text{TiO}_3$ ceramic which has a linear P - E relationship at room temperature (i.e., $P_r \approx 0$),¹⁷ the tested BST thin film possesses a significantly enhanced ferroelectricity along the in-plane direction. Such enhancement to the ferroelectricity along the in-plane direction, which is similar to the case of BST on MgO [which has a higher P_r ($\sim 9.5 \mu\text{C}/\text{cm}^2$)] could be attributed to a higher tetragonality.³

The lattice distortion in BST has also resulted in a significant shift of its Curie temperature (T_C). Figure 4 shows the temperature dependence of the dielectric constant of BST thin film. The Curie temperature of the BST film is found to be at $\sim 78^\circ\text{C}$, which is about 45°C higher than that of the $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ ceramic ($T_C=33^\circ\text{C}$, also shown in Fig. 4).¹⁸

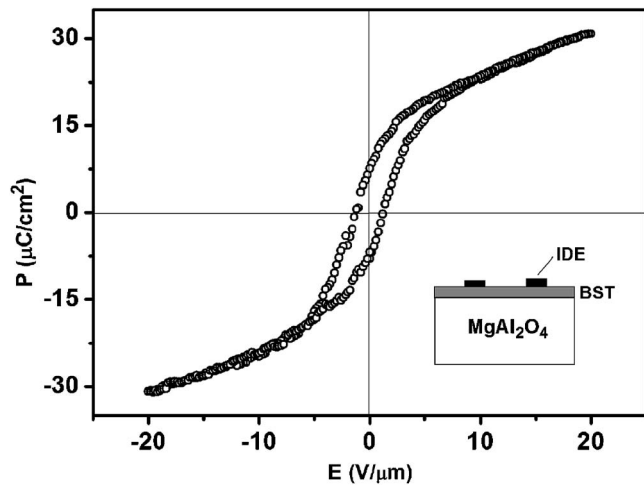


FIG. 3. In-plane ferroelectric hysteresis loop of $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ thin film grown on MgAl_2O_4 . The inset shows the schematic structure of the interdigital capacitor for measurement.

The shift of T_C in the tested BST thin film is not as significant as that observed in BaTiO_3 and SrTiO_3 thin films.^{1,2} One possible explanation for the difference could be that our tested film contained quite a number of dislocations (as observed under TEM) which have partially released the tensile stress caused by the lattice mismatch.⁵ The normalized dielectric constant $\epsilon_N = [\epsilon \text{ under bias}] / [\epsilon \text{ under zero bias}]$ versus dc bias field E of the BST film is shown in the inset of Fig. 4. Butterfly shaped ϵ - E curves were observed. The BST has displayed a good in-plane dielectric tunability, which is up to 30% under a dc field of $15 \text{ V}/\mu\text{m}$. These results can be regarded as confirmation to the enhanced ferroelectricity in the thin film and an implication that the heterostructure of BST/ MgAl_2O_4 can be used for tunable microwave components (phase shifters, filters, etc). The dielectric loss of the

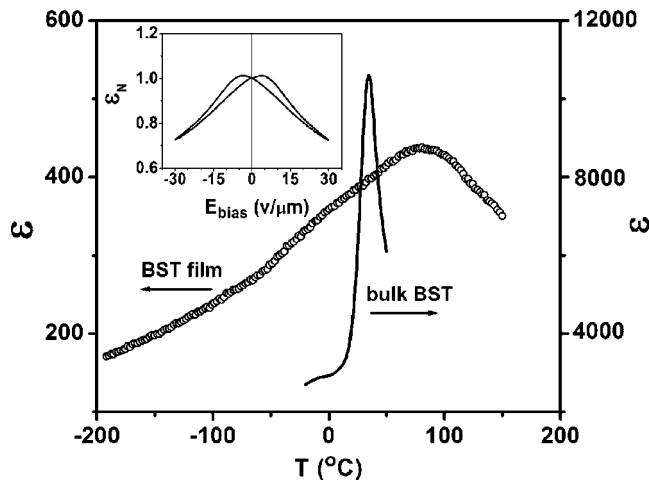


FIG. 4. Temperature dependence of the dielectric constant of $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ thin film (in plane) grown on MgAl_2O_4 and $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ ceramics. The data for the ceramic were after Ref. 16. The inset shows the dependence of the normalized dielectric constant on dc bias of the $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ thin film.

interdigital capacitor was also measured (data not shown). The value of $\tan \delta$ was found to be dependent on the temperature and dc bias and change from $\sim 0.2\%$ to 4% .

In summary, the structure, in-plane dielectric, and ferroelectric properties of $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ thin film grown on MgAl_2O_4 (001) single-crystal substrates have been investigated. It was found that the lattice mismatch has caused a lattice distortion in BST, making the thin film to have a tetragonal crystal structure, leading to an enhanced ferroelectricity (in-plane remnant polarization of $\sim 7.1 \mu\text{C}/\text{cm}^2$) at room temperature and an $\sim 45^\circ\text{C}$ shift of Curie temperature when compared with the $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ ceramic.

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