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Atomic structure of $Ba_{0.5}Sr_{0.5}TiO_3$ thin films on $LaAlO_3$

H.-J. Gao[a)]
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6030

C. L. Chen
Department of Physics and the Texas Center for Superconductivity, University of Houston, Houston, Texas 77204

B. Rafferty and S. J. Pennycook[b)]
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6030

G. P. Luo and C. W. Chu
Department of Physics and the Texas Center for Superconductivity, University of Houston, Houston, Texas 77204

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Perovskite barium strontium titanate $Ba_{0.5}Sr_{0.5}TiO_3$(BST) thin films were grown on (001) $LaAlO_3$ (LAO) using pulsed-laser ablation. The microstructures of the *as*-grown BST films were studied with selected electron diffraction, transmission electron microscopy, and scanning transmission electron microscopy. The BST thin films are oriented with their [001] directions parallel to the ⟨102⟩ directions of the LAO. Both cross-sectional and plan-view studies show the BST films to be single crystals with smooth surfaces. The interfaces were seen to be atomically sharp by cross-sectional, high-resolution electron microscopy. The density of misfit dislocations was consistent with the 4.3% lattice mismatch, and they were found to be dissociated into partials. *© 1999 American Institute of Physics.* [S0003-6951(99)00443-X]

Thin films of ferroelectric barium strontium titanates $(Ba_{1-x}Sr_x)TiO_3$ (BST) have recently become very attractive to the microelectronic industry as good candidates for device applications,[1] for example, as high density dynamic random access memories (DRAM),[2] smart card memories,[3] and tunable microwave devices.[4–9] They exhibit not only high values of the relative dielectric constant (ϵ_r), but also large tunability of ϵ_r through the application of an electric field. The tunability of BST thin films offers unique opportunities for the development of various microwave devices, such as microstrip line phase shifters, tunable filters, and high-Q resonators.

BST films with various stoichiometries have been grown on $LaAlO_3$ (LAO) by techniques such as sputtering, metal-organic chemical vapor deposition, laser ablation, and others.[10–13] LAO is also a widely used substrate for $PbZr_xTi_yO_3$ (PZT) films and for high temperature superconductors.[14–16] Application of BST to tunable microwave devices, however, requires high quality epitaxial BST films with atomically smooth surfaces and atomically sharp interfaces to minimize the loss tangent. Thus, investigating the microstructures between the as-grown films and the substrates and the epitaxial behavior is particularly important for BST thin film synthesis and device engineering. We have studied the microstructures and interface behavior of epitaxial BST films on (001) LAO by using selected area electron diffraction, transmission electron microscopy (TEM), and high resolution scanning transmission electron microscopy (STEM). In this letter, we present results from both cross-sectional and plan-view TEM studies of epitaxial BST films including the direct observation of dislocation cores at the interfaces between the films and substrates.

The BST samples used in this research were grown on (001) LAO by using pulsed laser deposition. Details on the growth procedure and the physical properties of the as-grown BST films can be found in the literature.[9] Briefly, the BST films are grown in oxygen pressures from 200 to 350 mTorr and at 750 to 830 °C to a thickness of typically 200 nm. X-ray diffraction indicates the films to be oriented with the [001] directions parallel to the ⟨102⟩ directions of the rhombohedral LAO. As the cell of LAO is close to cubic, this orientation is equivalent to a cube-on-cube orientation for a cubic substrate. Rocking curve measurements indicate a full width at half maximum (FWHM) of 0.15°. Samples for cross-sectional TEM studies were prepared using a standard procedure consisting of gluing, cutting, mechanical polishing, dimpling, and ion milling. Plan-view specimens were simply prepared by mechanical polishing and dimpling to thin out the substrate, followed by Ar-ion milling. Both plan-view and cross-sectional samples were ion milled by using an E.A. Fichione Ion Polishing System with an initial acceleration voltage of 3.5 kV, reducing to 1.0 kV at the end. Electron microscopy was carried out using a Philips EM-400 electron microscope operated at 100 kV for bright field images and selected area electron diffraction (SAED) patterns and a VG HB603 STEM at 300 kV for Z-contrast high-resolution images.

Figure 1 shows a bright field TEM image of a plan-view BST sample [Fig. 1(a)] and the selected area electron diffraction pattern taken from the same sample [Fig. 1(b)]. As seen in Fig. 1(a), the film consists of aligned rectangular-shaped

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[a)] On leave from Beijing Laboratory of Vacuum Physics, Institute of Physics & Center for Condensed Matter Physics, Chinese Academy of Sciences, Beijing 100080, P.R. China.

[b)] Electronic mail: pky@ornl.gov

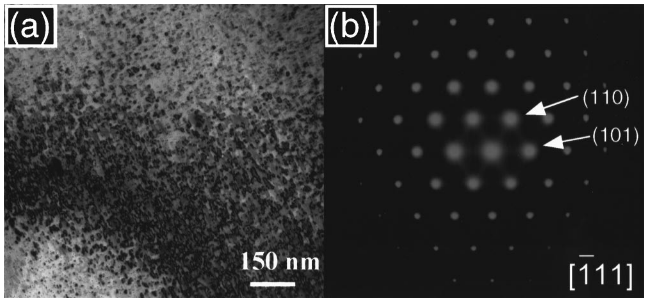

FIG. 1. TEM micrograph (a) and corresponding electron diffraction pattern (b) of a laser ablation deposited $Ba_{0.5}Sr_{0.5}TiO_3$ thin film, showing the formation of a single crystalline $Ba_{0.5}Sr_{0.5}TiO_3$ film. The electron projection is along the $\langle 111 \rangle$ zone axe of the $Ba_{0.5}Sr_{0.5}TiO_3$ thin film.

domains formed during the film growth. The SAED pattern was taken along the BST [111] direction. The sharp diffraction spots show that the *as*-grown BST films are good single crystals.

In order to understand better the film quality and the epitaxial behavior of the BST films on (001) LAO substrates, investigations of cross-sectional specimens were conducted using electron diffraction, bright field imaging, and *Z*-contrast imaging. Figure 2(a) is a low magnification bright field TEM image of the cross-sectional sample. The as-grown film has a flat surface with about 1 nm roughness, a sharp interface with the substrate, and a very uniform thickness of about 200 nm over the entire specimen. The columnar texture is due to small rotations between the grains, and is consistent with the FWHM of the x-ray rocking curve results. No large angle grain boundaries were found in the entire cross-sectional sample, indicating a near perfect single crystal BST film. Figure 2(b) is a SAED pattern taken in the area covering both the film and the substrate and along a [010] direction of the LAO (using pseudocubic notation). The superposition of patterns from the BST film and the LAO substrate is indexed in Fig. 2(c). The ''cube-on-cube'' orientation is clearly observed with the epitaxial relationship $[010]_{BST} \| [010]_{LAO}$ and $(101)_{BST} \| (101)_{LAO}$. The lattice mismatch was estimated to be about 4.5% from the high order spots in the diffraction patterns, which is in good agreement with the BST and LAO lattice parameters. This result implies that the film is fully relaxed, with edge dislocations between the film and the substrate every 22 unit cells along the BST [100] direction.

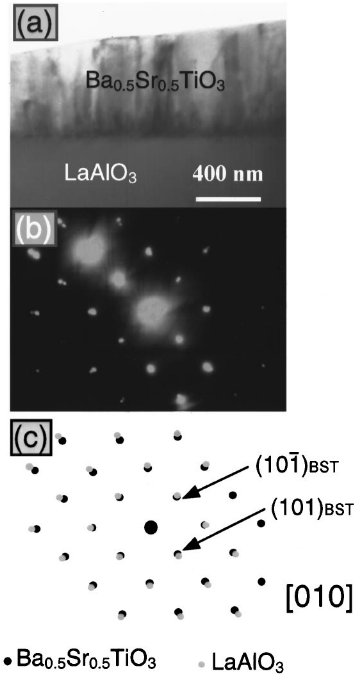

FIG. 2. TEM micrograph (a) and corresponding electron diffraction pattern (b) of both the substrate and the grown $Ba_{0.5}Sr_{0.5}TiO_3$ film. The crystalline orientation relation of the substrate and the film is deduced in (c).

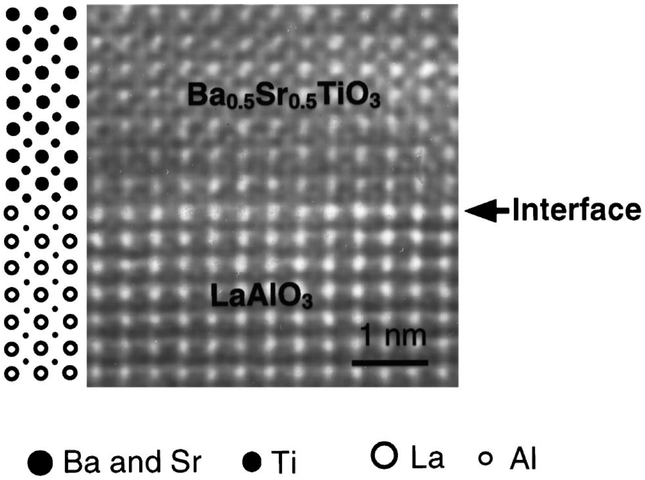

FIG. 3. *Z*-contrast STEM dark field image of the interface structure between the substrate $LaAlO_3$ and the grown $Ba_{0.5}Sr_{0.5}TiO_3$ film. Atom column positions can be clearly seen in both the substrate and the film, as shown in the schematic.

High-resolution, cross-sectional electron microscopy studies of the as-grown films provide detailed information on the atomic structure of the interface. Figure 3(a) shows a *Z*-contrast STEM[17,18] image taken along the $[010]_{LAO}$ zone axis, that shows the interface between the film and the substrate is atomically sharp and flat. The stacking sequence across the interface is clearly visible. The last plane of the substrate is seen to be the La plane, while growth of the BST is seen to initiate with the Ti plane. No precipitates or other phases are present in the film or at the interface.

Edge dislocations were seen periodically along the entire interface, with a period of the edge dislocations of about 22 unit cells in BST lattice or 23 unit cells in the LAO lattice, which is in good agreement with the 4.3% lattice mismatch. This confirms that the BST film is essentially fully relaxed. Figure 4(a) shows a *Z*-contrast STEM image of the interface between LAO and the BST, with the approximate locations of misfit dislocation cores arrowed. Their cores lie a few unit cells inside the BST film. Between the cores the $Ba_{0.5}Sr_{0.5}$ plane of the BST is matched to the La plane of the LAO, and the Ti with the Al, as expected. Even in thin regions the misfit dislocation cores did not show the clear reconstructed form seen in $SrTiO_3$ grain boundaries[19] and $SrTiO_3/SrZrO_3$ interfaces.[20] As seen in the higher magnification images of Fig. 4(b), there is a strong tendency for the dislocations in this material to decompose into partials, $a[100] \rightarrow a/2[101] + a/2[10\text{-}1]$.

It should be pointed out that no twins were observed

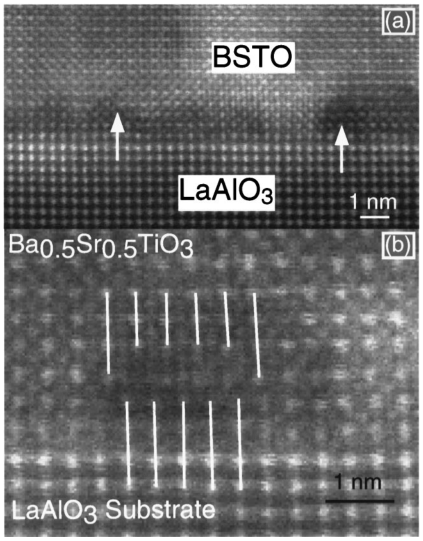

FIG. 4. (a) *Z*-contrast STEM dark field image of the interface between the substrate $LaAlO_3$ and the $Ba_{0.5}Sr_{0.5}TiO_3$ film showing misfit dislocation spacing, (b) high-resolution *Z*-contrast image showing a misfit dislocation decomposed into two partial dislocation cores separated by a small segment of stacking fault. The cores are located ~3 unit cells inside the film.

inside the BST films grown under these conditions. Threading dislocations must be present at the small angle grain boundaries between the columnar grains. Using the 0.15° FWHM and the ~50 nm grain size observed from TEM, a dislocation density of approximately $2\times10^9\,\mathrm{cm}^{-2}$ is estimated. Therefore the BST films have excellent single crystal quality. Although it is not well understood how the physical properties of high quality BST films relate to their microstructures, we would anticipate that single crystal films of this quality should display similar behavior and physical parameters with bulk materials. This is why the as-grown BST films exhibit a very high dielectric constant ϵ_r of about 1500 that is competitive with that of BST bulk single crystals, a large tunability of 33% under an electric field of 2.33 V/μm at room temperature, and very low loss tangent δ of only about 0.007.[9]

In summary, single crystalline $Ba_{0.5}Sr_{0.5}TiO_3$ thin films epitaxially grown on (001) LAO by pulsed laser deposition were characterized by SAED, TEM, and STEM. The as-grown films had a columnar structure, with an orientation relationship of $[010]_{BST}\|[010]_{LAO}$ and $(100)_{BST}\|(100)_{LAO}$. *Z*-contrast STEM images reveal the misfit dislocations to be dissociated, but the interfaces were seen to be atomically smooth and atomically abrupt.

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