

## Threading dislocation generation in epitaxial (Ba,Sr)TiO<sub>3</sub> films grown on (001) LaAlO<sub>3</sub> by pulsed laser deposition

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Epitaxial Ba<sub>0.6</sub>Sr<sub>0.4</sub>TiO<sub>3</sub> films were grown onto (001) LaAlO<sub>3</sub> by pulsed-laser deposition, and the dislocation structures of the films were investigated using transmission electron microscopy. Misfit dislocations with a periodicity of about 7 nm and Burgers vectors  $\mathbf{b} = a\langle 100 \rangle$  were observed at the interface. A high density of threading dislocations was present in the films and these also had  $\mathbf{b} = a\langle 100 \rangle$ . The data indicate that the threading dislocations are not generated as the result of half-loop climb from the deposit surface as proposed previously, but are instead formed when misfit dislocations are forced away from the interface during island coalescence. © 2004 American Institute of Physics. [DOI: 10.1063/1.1664035]

The effects of microstructural features such as grain boundaries and structural (90°) domains on the physical and dynamic properties of ferroelectric films have been studied extensively. There has, however, been very little work on the effects of the dislocations present in these films. In a recent study,<sup>1</sup> it was shown that the dielectric response in epitaxial ferroelectric films is strongly dependent on the dislocation microstructure.

Dislocations in heteroepitaxial thin films can be divided into two types: misfit and threading dislocations [(MDs) and (TDs), respectively]. MDs lie in the epitaxial interface and accommodate the lattice mismatch between the film and substrate. For metallic and semiconductor films, the mechanisms by which MDs can be introduced are now well understood. For deposits that grow in the 3D Volmer–Weber mode, this usually occurs by the introduction of edge dislocations at island edges during growth.<sup>2</sup> For deposits growing in the 2D Frank–Van der Merwe mode, however, this cannot occur and misfit dislocations are often introduced as glissile half-loops either from the deposit surface or from regenerative dislocation sources in the deposit.<sup>3</sup> TDs lie within the film and run from the interface to the film surface and were originally explained on the basis of dislocation “copying” wherein dislocations in the substrate were duplicated into the deposit when they were overgrown.<sup>4,5</sup> It has been shown subsequently that this mechanism cannot be used to explain most of the TDs in epitaxial deposits since the density typically exceeds that of the dislocations in the substrate by several orders of magnitude.<sup>3,6–8</sup> The “excess” TDs must, therefore, be introduced into the film during growth. There is now a clear consensus that this occurs by the glide of half-loops generated in response to misfit stresses at the interface, and that the final configuration consists of a misfit segment lying in the interfacial plane bounded by two segments that thread

from the interface to the deposit surface, in the manner first described by Matthews.<sup>9</sup>

Although the evolution of TD and MD microstructures has been studied extensively for heteroepitaxial semiconductor films, little is known about the corresponding processes for ferroelectric perovskite deposits. Attempts to characterize dislocations in ferroelectric thin films have been confined to the efforts of a few groups.<sup>6–8,10–13</sup> In one of the most extensive studies, (001) BaTiO<sub>3</sub> on (001) SrTiO<sub>3</sub> was investigated by Suzuki *et al.*<sup>7</sup> These authors reported both TDs and MDs with Burgers vectors of  $a\langle 100 \rangle$  parallel to the substrate surface, and inferred that misfit relaxation occurred by the introduction of half-loops with these Burgers vectors. We note, however, that there is no resolved shear stress on such defects from the lattice misfit and hence the expansion of the half-loops to the interface would have to occur by climb alone. The deposition rates used in these experiments were not quoted by the authors, but for typical pulsed laser deposition (PLD) parameters at the deposition temperature used (700 °C) the diffusivities are far too low for such processes to contribute significantly to misfit relaxation. In our work, we have revisited this issue by performing transmission electron microscopy (TEM) studies on the dislocation structures in heteroepitaxial films of barium strontium titanate (BST) grown by PLD on various substrates. In this letter we report data obtained from Ba<sub>0.6</sub>Sr<sub>0.4</sub>TiO<sub>3</sub> films grown onto (001) LaAlO<sub>3</sub> single crystal substrates. It is shown that the density and distribution of the TDs are not consistent with the half-loop mechanism described by Suzuki *et al.*,<sup>7</sup> but can instead be explained by MD segments being forced away from the interface during island coalescence.

BST films of three different thicknesses (100, 300, and 500 nm) were deposited by PLD from a sintered BST target using growth conditions that have been shown previously<sup>1</sup> to result in high quality epitaxial films with the orientation: (001)<sub>BST</sub>//(001)<sub>substrate</sub> and [100]<sub>BST</sub>//[100]<sub>substrate</sub>. X-ray diffraction was used to confirm that the films were single crystal with the orientation expected and contained no sec-

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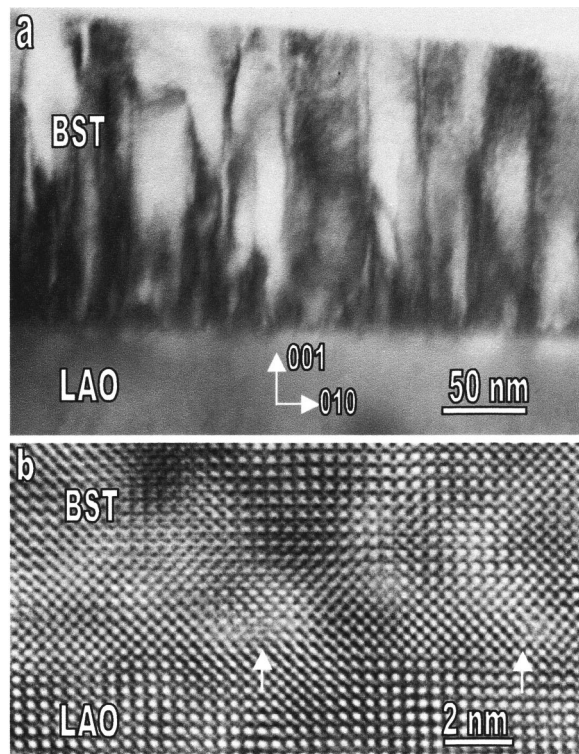


FIG. 1. TEM images obtained from cross-sectional specimens of the 300 nm film at the [010] zone axis: (a) bright field image; (b) HRTEM image of MDs at the interface.

ondary phases. Both plan-view and cross-sectional TEM specimens were produced in the usual manner by mechanical prethinning followed by Ar ion-beam milling to perforation. Diffraction contrast images were obtained from the samples in a Philips EM420 TEM operating at 100 kV. High-resolution TEM (HRTEM) images were obtained in a JEOL 2010 FasTEM operating at 200 kV. This latter instrument is equipped with a high-resolution objective lens pole-piece ( $C_s=0.5$  mm) giving a point-to-point resolution of  $<0.19$  nm in phase contrast images.

Similar microstructures were observed in each of the three films, and for brevity we present here only images obtained from the 300 nm film. Diffraction contrast TEM images obtained from the cross-sectional specimens revealed that the films contained a high density of TDs [e.g., Fig. 1(a)] and HRTEM images from these specimens revealed a periodic array of MDs in the interface plane [e.g., Fig. 1(b)]. These MDs were spaced regularly with a separation of  $\approx 7$  nm and circuit mapping showed that, in each case, they were edge-type with  $\mathbf{b}=a[100]$ . The spacing and character of these MDs did not vary from area to area within the specimen, or from one specimen to another, i.e., there was no effect of film thickness on MD content for these deposits. The observed MD arrays are consistent with those required to accommodate the lattice misfit of 4.7% between  $\text{Ba}_{0.6}\text{Sr}_{0.4}\text{TiO}_3$  and stoichiometric  $\text{LaAlO}_3$ . The distribution of the TDs was revealed more clearly in diffraction contrast images from plan-view specimens [Fig. 2(a)] and the TD density measured from such images was  $\approx 7 \times 10^{10} \text{ cm}^{-2}$  in each of the three samples. The character of the TDs was revealed most clearly in HRTEM images [e.g., Fig. 2(b)]. Here again, circuit mapping revealed that all of the TDs were

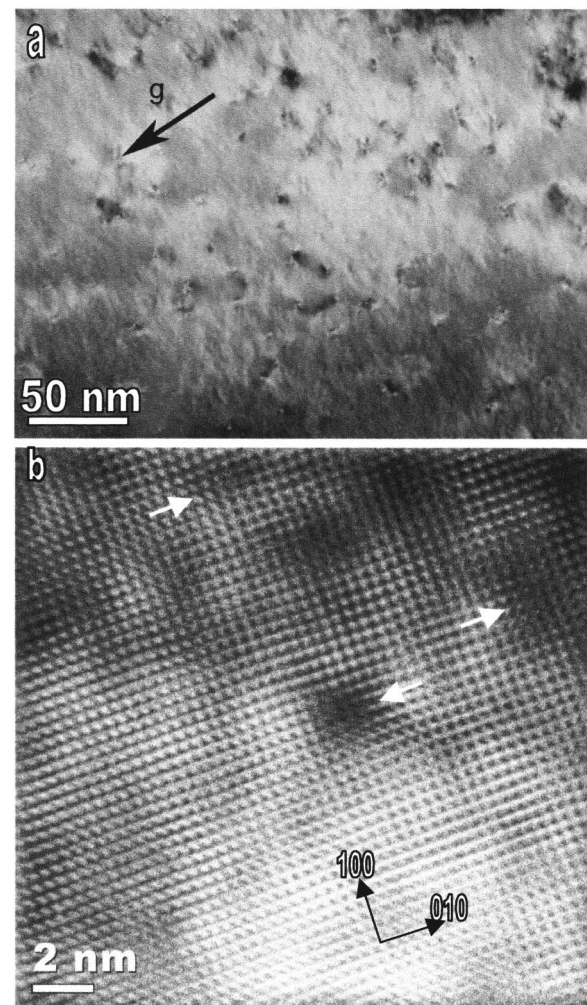


FIG. 2. TEM images from plan-view specimens of the 300 nm film: (a) bright field image of the TD distribution obtained with  $\mathbf{g}=100$ ; (b) HRTEM image with TD cores indicated by arrows.

edge-type with  $\mathbf{b}=a[100]$ . We note that all of the TDs had compact cores with no evidence for any dissociation such as that reported by Lu *et al.*,<sup>8</sup> although these observations are not necessarily contradictory since the films studied by these authors were of a different composition.

Since there is no significant effect of film thickness on dislocation structure in these samples, it is clear that the introduction of MDs must have occurred at a thickness well below 100 nm. The observations presented here are broadly consistent with the data reported by Suzuki *et al.*,<sup>7</sup> in that all of the MDs and TDs are edge type with Burgers vectors  $\mathbf{b}=a\langle 100 \rangle$  lying parallel to the interface. If the dislocations were introduced into an initially pseudomorphic continuous deposit growing in the 2D Frank–Van der Merwe mode, then it would be necessary to invoke a climb-based introduction of dislocation half-loops at the deposit surface. While this would account for the character of both the MDs and TDs in these deposits, the diffusive fluxes required seem unfeasible at such a low homologous temperature ( $<0.5 T_m$ ), and to the authors' knowledge there are no other examples in the literature in which climb-based misfit dislocation introduction has been proposed. To refute this mechanism on the basis of the diffusive fluxes required is, however, rather challenging both because of the complex multicomponent diffu-

sion mechanisms that occur in such oxides and because of the paucity of accurate diffusivity data. What leads us to believe that climb rates are insufficient to produce the MDs in this system is that the density of the TDs does not vary with film thickness over the range considered in this study. At densities of  $>10^{10} \text{ cm}^{-2}$  the distance between the TDs is low enough that the magnitudes of elastic interactions between adjacent threading segments will be significant. If the MDs (and thus the TDs) were introduced by climb of dislocation half-loops to the interface at some deposit thickness less than 100 nm, then one would expect the TDs to have sufficient mobility that adjacent segments could interact during subsequent growth. Where the forces between these segments are attractive, the interaction would lead to the combination or mutual annihilation of adjacent segments, giving a decrease in TD density with increasing film thickness.<sup>14</sup> Since this is not observed experimentally, we infer that the TDs are relatively immobile and thus it is implausible that these features arise as a result of climb of half-loops.

To explain the dislocation microstructure observed experimentally, we propose that the BST deposits form initially as islands growing in the 3D Volmer–Weber mode, as one might expect for a deposit with a misfit of 4.7%. For Volmer–Weber growth, edge-type MDs are usually introduced periodically at the periphery of the growing islands to minimize the strain in the deposit. The Burgers vectors and character of the MDs observed experimentally, and the regularity of the MD arrays is entirely consistent with such a mechanism. To explain the high densities of TDs, we recall some of the earliest work on epitaxy of metals, wherein it was shown that TDs can form when adjacent islands which are misaligned and/or misoriented with respect to one another coalesce.<sup>5</sup> This results in some of the MDs being forced away from the interface. Studies on certain other heteroepitaxial oxide on oxide systems grown by PLD have shown that islands with substantial misorientations can be deposited while still resulting in single-crystal epitaxial films

after coalescence. Thus, if the density of island nuclei were high enough, and coalescence were to occur at an early stage in the growth, then a high density of TDs could arise with Burgers vectors parallel to the interface, as observed experimentally. Moreover, if the mobility of the TD segments were low enough then these would simply extend in length as the deposit grows, irrespective of the nature of any elastic interactions with adjacent segments. This could result in a TD density that did not vary with film thickness. Clearly, further work is required to test these hypotheses and to this end investigations on the initial stages of growth and the effects of postdeposition annealing on TD distribution are underway.

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