Unusual lattice distortion in a $Ba_{0.5}Sr_{0.5}TiO_3$ thin film on a $LaAlO_3$ substrate

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Transmission electron microscopy (TEM) of a perovskite $Ba_{0.5}Sr_{0.5}TiO_3$ thin film, grown on a (001) $LaAlO_3$ substrate by pulsed-laser ablation, reveals that the film of single-crystal quality has an unusually distorted lattice with lattice parameters a and b (parallel to the interface) larger than c (perpendicular to the interface) by 1.4%. There is evidence that the as-examined $Ba_{0.5}Sr_{0.5}TiO_3$ film is a variant of its high-temperature cubic phase due to its anisotropic thermal contraction during cooling. A large lattice mismatch value of 5.7% (to be compared to the normal value of 4.13%) is observed from selected area electron diffraction patterns and high-resolution TEM images of cross-sectional specimens, which suggests that the growing high-temperature film under the film growth condition may have a larger lattice constant and a different thermal expansion behavior with respect to the bulk material. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1500413]

Due to their large relative dielectric constant (ε_r) and the high tunability of ε_r through the application of an electric field, perovskite solid solution $Ba_xSr_{1-x}TiO_3$ thin films are now becoming more and more attractive to the microelectronics industry.[1–4] $Ba_xSr_{1-x}TiO_3$ thin films are important potential candidates for a variety of technologies, for example, as high density dynamic random access memories, smart card memories and microwave devices.[3,5–7] Recently, epitaxial ferroelectric $Ba_xSr_{1-x}TiO_3$ thin films, deposited on $LaAlO_3$ and MgO substrates by pulsed-laser ablation, have been demonstrated to exhibit excellent and variable dielectric properties, which offers unique opportunities for the development of various high performance microwave devices, such as micro strip line phase shifters, tunable filters, steerable antennas etc.[1,2,8,9]

It is known that the properties of thin films depend on their chemical composition and microstructure, and the microstructure in turn depends on the fabrication process. Thus, the study of the microstructural features in $Ba_xSr_{1-x}TiO_3$ films provides important information for understanding film properties and for fabricating high quality films. For example, the density of interfacial dislocations directly reflects the degree of film relaxation.[10] Systematic studies indicate that the films grown at oxygen pressures in the range of 200 to 250 mTorr and at temperatures higher than 800 °C have excellent dielectric properties with the dielectric constant as high as 2130 and a very low dielectric loss of 0.005 at room temperature. Using high resolution TEM (HRTEM), selected area electron diffraction (SAED) and energy dispersive x-ray spectroscopy (EDX), we have investigated the microstructure of epitaxial $Ba_xSr_{1-x}TiO_3$ thin films with different compositions, deposited on $LaAlO_3$ substrates by pulsed-laser ablation. In this letter, we report an unusual lattice distortion in a $Ba_{0.5}Sr_{0.5}TiO_3$ thin film on a (001) $LaAlO_3$ substrate. The observed microstructural features directly reflect some unknown behavior of $Ba_xSr_{1-x}TiO_3$ films in the film fabrication process.

The examined $Ba_{0.5}Sr_{0.5}TiO_3$ film was grown on a (001) $LaAlO_3$ substrate by pulsed-laser ablation in an oxygen pressure of 200 mTorr and at a temperature of 830 °C to a film thickness of 900 nm, and then post-annealed at near one atmosphere oxygen pressure and 830 °C for 30 min. The detailed growth procedure can be found in the literature.[1] For bulk materials, $LaAlO_3$ has a pseudocubic cell with lattice parameter $a=0.379$ nm[11] and $Ba_{0.5}Sr_{0.5}TiO_3$ has a cubic cell with $a=0.395$ nm.[12] Cross-sectional specimens of this thin film for TEM investigations were prepared using the standard procedure consisting of cutting, gluing, mechanical polishing, and ion milling. Specimens were examined using a JEOL 4000 EX TEM for high-resolution images, bright-field images and SAED patterns. A Philips CM20 ST TEM was used for the EDX analysis.

Figure 1 shows a typical HRTEM image of the periodic misfit dislocations formed at the interface between the $Ba_{0.5}Sr_{0.5}TiO_3$ film and the $LaAlO_3$ substrate. These are pure edge dislocations with the Burgers vector $\mathbf{b}=[100]a$. Some of the misfit dislocations tend to decompose into partials, as reported in the literature,[10] but most of them remain undissociated. The most interesting feature seen in Fig. 1, however, is that the average period of the misfit dislocations is about 17.5 unit cells of the $LaAlO_3$ lattice, which reflects a 5.7% lattice mismatch. This value is much larger than the 4.13% expected from the lattice parameters of bulk materials and also the values reported in the literature.[1,10]

Performing numerical Fourier transform of the high-resolution images of cross-sectional specimens to obtain their diffractograms, we carried out further investigations on the large lattice mismatch phenomenon. A typical result is demonstrated in Fig. 2. Careful measurements of the diffractograms show the following: (i) the lattice mismatch between

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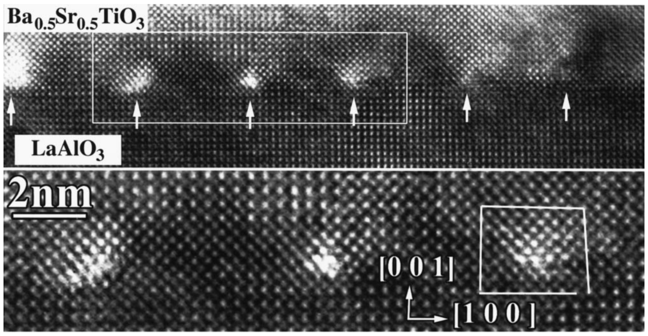

FIG. 1. Top: HRTEM image of the nearly periodically arranged misfit dislocations with the Burgers vector $\mathbf{b}=[1\,0\,0]a$ in the $Ba_{0.5}Sr_{0.5}TiO_3$ film. The average distance between two closest dislocations is about 17.5 unit cells in the $LaAlO_3$ lattice, reflecting a 5.7% lattice mismatch. Bottom: Magnified image of the selected area in the top image.

the film and the substrate is anisotropic. In the direction normal to the interface the mismatch is 4.2%, in agreement with the value of 4.13% for bulk materials, but it is 5.7% in the directions parallel to the interface, consistent with the estimation based on the density of interfacial dislocations. (ii) The $LaAlO_3$ lattice parameters parallel to the interface are equal to that perpendicular to the interface, indicating that the large mismatch is due to a lattice parameter change in the film. (iii) The $Ba_{0.5}Sr_{0.5}TiO_3$ lattice parameters a and b (parallel to the interface) are larger than c (perpendicular to the interface) by 1.4%. Obviously this demonstrates that the as-examined $Ba_{0.5}Sr_{0.5}TiO_3$ film has a distorted lattice with a $(=b)$ larger than c. Figure 2 also shows that a partial dislocation with $b=(1/2)[10\bar{1}]a$ appears between two normal [100] interface dislocations. Since the projection of $b=(1/2)[10\bar{1}]a$ to the interface is $(1/2)[100]a$, its contribution to the relaxation of mismatch strain is only half of that from a [100] interface dislocation. However, the mechanism for the formation of such individual partials at the interface is not clear.

In order to investigate whether or not the observed unusual lattice distortion is only a local phenomenon occurring near the interface, we used SAED to examine the entire film from the interface to the top of the film. Figure 3 shows a bright-field image of the film and two typical SAED patterns, one from the interface area and another from the top area of the film. The SAED patterns confirm that the entire film with a thickness of 900 nm is of single crystal quality and has a distorted lattice with $a(=b)$ larger than c by 1.4%.

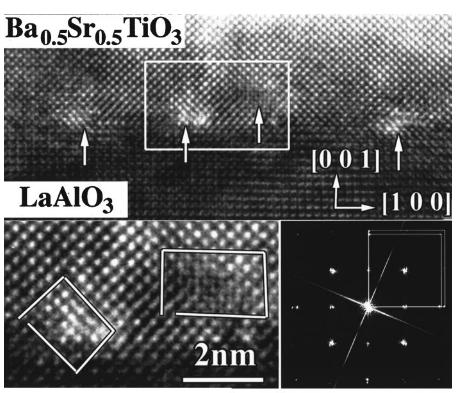

FIG. 2. HRTEM image of a cross-sectional $Ba_{0.5}Sr_{0.5}TiO_3$ specimen with two insets at the bottom. Bottom left: a magnified image of the selected area that contains two interfacial dislocations of different types: $\mathbf{b}=[100]a$ and $\mathbf{b}=(1/2)[10\bar{1}]a$; Bottom right: diffractogram of the image with a square indicating that the $(2\ 0\ \ell)$ $(\ell=0,1,...)$ reflections are located inside the square, while the (h02) $(h=0,1,...)$ reflections are located outside the square.

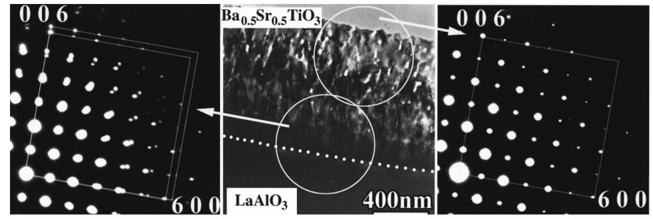

FIG. 3. Bright-field image (center) of a cross-sectional specimen and the corresponding SAED patterns (left and right). Left: the SAED pattern of an interface area that contains diffraction spots from both the $Ba_{0.5}Sr_{0.5}TiO_3$ film and the $LaAlO_3$ substrate; Right: the SAED pattern of a film top area in which only reflections from the film appear. Squares are drawn to show the difference between the lattice parameters a and c.

We sometimes observed small domains or precipitates that do not exhibit the abnormal lattice distortion. Figure 4 shows a high-resolution image of the $Ba_{0.5}Sr_{0.5}TiO_3$ film viewed along the $[\bar{1}10]$ direction. Two precipitate-like domains (marked by **c**) can be seen near the interface. The inserted diffractogram of the image reveals three sets of reflections, corresponding to three different crystal lattices: the $LaAlO_3$ lattice marked by **a** in the diffractogram, the unusually distorted $Ba_{0.5}Sr_{0.5}TiO_3$ lattice (indicated by **b**) and the domain lattice marked by **c**. Detailed measurements show that in both the directions parallel and perpendicular to the interface the lattice mismatch between the $LaAlO_3$ and **c** domains is 4.2%, which is consistent with the expected value of 4.13% for the normal $Ba_{0.5}Sr_{0.5}TiO_3$ lattice. This implies that the two **c** domains or precipitates have a normal cubic $Ba_{0.5}Sr_{0.5}TiO_3$ lattice.

It should be pointed out that in our experiments the observed interface dislocations are not perfectly periodic, especially when the boundaries of the growth columns and precipitate-like domains appear, as seen in Figs. 2 and 4. The measured average distances between two dislocations, however, are always about 17.5 unit cells in the $LaAlO_3$, consistent with the mismatch values given by the diffractograms and SAED patterns. In the well-grown areas of the film the periodicity of the dislocations tends to be more ''perfect,'' as seen in Fig. 1. For the $LaAlO_3$ substrate no lattice distortion has been observed. If $a=0.379$ nm is assumed for the $LaAlO_3$ lattice,[11] the lattice parameters of the unusually distorted $Ba_{0.5}Sr_{0.5}TiO_3$ film can be estimated from the observed mismatch values to be $a=b=0.401$ nm and $c=0.395$ nm. This result indicates that the unit cell of the $Ba_{0.5}Sr_{0.5}TiO_3$ thin film is larger than that of the bulk material. The large free space allows ions in the unit cell to be easily polarized under an electric field and consequently will lead to a high dielectric constant. This is why we are able to achieve the dielectric constant as high as 2130.

Apparently the observed film lattice is not a lattice-mismatch-induced strained variant of the normal cubic $Ba_{0.5}Sr_{0.5}TiO_3$ structure with $a=b=c=0.395$ nm, since in that case the compressive stress in the film (because of the larger lattice parameters of $Ba_{0.5}Sr_{0.5}TiO_3$ with respect to that of $LaAlO_3$) should lead to a strained lattice with $a(=b)$

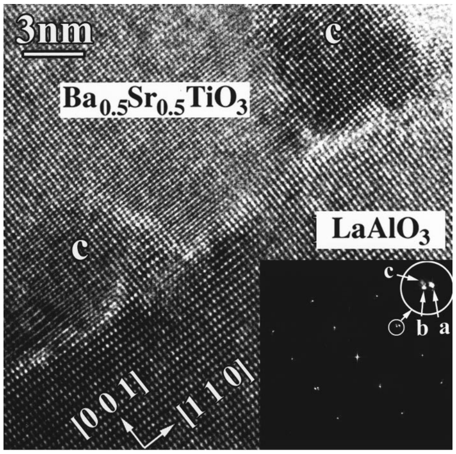

FIG. 4. RTEM image of a cross-sectional $Ba_{0.5}Sr_{0.5}TiO_3$ specimen viewed along the $[\bar{1}10]$ direction, showing two precipitate-like domains (marked by **c**) near the interface. The inset is the diffractogram of the image.

smaller than c. Hence the unusual lattice distortion observed here reflects an unknown growth behavior of the $Ba_xSr_{1-x}TiO_3$ film. The reasons for the observed distortion are not very clear, because of the lack of some basic experimental data concerning the physical properties and the structure of the material. For example, the exact thermal linear expansion coefficients of $LaAlO_3$, $BaTiO_3$ and $SrTiO_3$ are unknown for high temperatures. Although no compositional inhomogeneity has been detected in our EDX measurements, more accurate methods are needed in order to detect whether or not there is a local compositional change at nanometer scale.

To our knowledge, if the compositional fluctuations are the reason for such a lattice distortion, the mechanism by which the unit cell is stretched should be profound. This is because the distortion occurs only in the directions parallel to the interface. For example, assuming that there might be more Ba than Sr in the film, we could explain the large mismatch value of 5.7% in the interface plane, but could not interpret the normal mismatch of 4.2% in the direction perpendicular to the interface.

On the other hand, it is logical to speculate that the distorted lattice observed here is a variant of a high-temperature cubic $Ba_{0.5}Sr_{0.5}TiO_3$ lattice with its thermal contraction during cooling restricted in the directions parallel to the interface. This speculation consists of two related points. The first point is that the large lattice mismatch of 5.7% has occurred under the film growth condition. In other words, the growing high-temperature film could be in a nonequilibrium state and have a lattice constant larger than the value of the $Ba_{0.5}Sr_{0.5}TiO_3$ bulk material at the same temperature (about 830 °C). Since the lattice parameter and the average thermal linear expansion coefficient of the $LaAlO_3$ substrate are 0.379 nm (at room temperature) and $10\times10^{-6}\,°C^{-1}$ respectively,[13] the lattice parameter of the substrate at 830 °C will be about 0.382 nm. The high-temperature film should have a lattice constant of 0.404 nm for a mismatch of 5.7%. On the other hand, the estimated lattice parameter of the $Ba_{0.5}Sr_{0.5}TiO_3$ bulk material at 830 °C is about 0.398 nm, with its linear thermal expansion coefficient estimated to be $10\times10^{-6}\ K^{-1}$ (for both $BaTiO_3$ and $SrTiO_3$ the coefficient is about $10\times10^{-6}\ K^{-1}$,[13,14]). Hence, in order to achieve the mismatch of 5.7% we have to assume that the thermal expansion behavior of the high-temperature film is very different from the $Ba_{0.5}Sr_{0.5}TiO_3$ bulk materials. The second point is that the film contraction is restricted by the appearance of interface dislocations. If there was no restriction, the high-temperature film lattice would contract to the normal cubic $Ba_{0.5}Sr_{0.5}TiO_3$ lattice on cooling. This is supported by the fact that in the direction perpendicular to the interface the film indeed has a normal mismatch of 4.2%. However, in the direction parallel to the interface the film must follow the contraction of the substrate in order to maintain the number of interface dislocations. Further contraction of the film to normal lattice parameters requires the removal of 24% of the total number of interface dislocations and this would require an enormous amount of energy. This also implies that the large mismatch observed is generated under grow conditions.

In summary, using HRTEM and SAED, a $Ba_{0.5}Sr_{0.5}TiO_3$ film with excellent dielectric properties has been characterized as a distorted lattice with its lattice parameters $a(=b)$ (parallel to the interface) larger than c (perpendicular to the interface) by 1.4%. There is evidence that the unusually distorted structure is a variant of a high temperature cubic $Ba_{0.5}Sr_{0.5}TiO_3$ film due to its anisotropic thermal contraction during cooling. The observed large lattice mismatch suggests that the high temperature cubic phase of the $Ba_{0.5}Sr_{0.5}TiO_3$ film under growth conditions may have a lattice parameter much larger than the value given for bulk materials, and consequently a different thermal expansion (or contraction) behavior in comparison with bulk materials.

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