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Growth and Characterization of Ferroelectric $LaTiO_{3.5}$ Thin Films

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Abstract

Depending upon the oxygen content x, $LaTiO_{3+x}$ *can be a semiconductor, a metal, or a ferroelectric at room temperature. Using a thin-film approach, it is in principle possible to adjust the oxygen content in the growth direction and thus tune the electronic properties within the same sample. We report here on a systematic study of the epitaxial growth of* $LaTiO_{3.5}$ *films on* $SrTiO_3$ *(110) substrates using molecular beam epitaxy. The epitaxial behaviour and the growth mechanism of these films have been investigated by means of X-ray diffraction, transmission electron microscopy, and* in situ *reflection high-energy electron diffraction analysis.* © *1999 Elsevier Science Limited. All rights reserved*

Keywords: films, electron microscopy, X-ray methods, ferroelectric properties, perovskites.

1 Introduction

Many interesting properties of perovskite-type compounds ABO_3 arise because the transition element B can take a mixed valency.[1,2] The perovskite $LaTiO_3$ belongs to this class, and its chemistry has been proved to be highly flexible.[3–6] In particular, the physical phase diagram has been extensively studied as a function of oxygen doping $0 < x < 0{\cdot}5$.[7] A metallic, semiconductor, or ferroelectric behavior is observed at room temperature, depending on the x value. For low oxygen contents, $0 < x < 0{\cdot}2$, the crystal structure consists of a three-dimensional $[TiO_6]$ octahedra network. For $x = 0{\cdot}5$, all the additional oxygen atoms are ordered on infinite $\{110\}_{\text{perovskite}}$ planes, with a periodic stacking distance of 1·28 nm ('4 octahedra blocks').[8] This compound (Fig. 1) is ferroelectric[9] with one of the highest reported T_c (1500°C), and offers interesting perspectives for applications. Prior to any of these studies, the growth of high-quality $LaTiO_{3+x}$ thin films must however be mastered and understood. For $x = 0{\cdot}5$, few results have been reported,[10,11] and to our knowledge epitaxial growth has not been achieved previously.

2 Experimental Details

Epitaxial thin films are prepared in a molecular beam epitaxy (MBE) system using the block-by-block deposition method.[12] They are grown at 800 ± 10°C on $SrTiO_3$ (110) (STO), under a flow of atomic oxygen produced by an RF-plasma source. This substrate orientation provides the only surface with coincident sites for the growth of $LaTiO_{3.5}$. Furthermore, the in-plane lattice mismatch is very small, i.e. −0·47 and 0·12% along both orthogonal directions. Lanthanum and titanium are evaporated from electron sources, and the deposition sequence consists of a La–O_x monolayer followed by the deposition of a Ti–O_x monolayer. The oxygen background pressure is $1{\cdot}5 \times 10^{-5}$ Torr before deposition, and decreases to 3×10^{-6} Torr as a function of the (La, Ti) evaporation rates. After growth, the films are cooled down under atomic oxygen at a rate of 10°C min^{-1}. The structural quality of these films is monitored *in situ* by reflection high-energy electron diffraction (RHEED), and *ex situ* by X-ray diffraction on a Siemens D500 diffractometer equipped with a graphite back monochromator. For the transmission electron microscopy (TEM) study, plan-view and cross-section samples were prepared by cutting, grinding and finallly thinning with an Ar-ion beam to electron transparency. High-resolution TEM (HRTEM) studies were performed in a Jeol 4000EX (point-to-point resolution of 1·7 Å) and a Jeol 4000FX microscope operating at 400 kV.

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3 Results

3.1 Crystal structure of the films

The $\theta - 2\theta$ X-ray diffractogram of a film grown on STO is shown in Fig. 1. At low 2θ angles, finite-size oscillations can be observed around the film diffraction peaks. They indicate a good structural coherence through the entire film and a crystalline film thickness of $12{\cdot}5 \pm 1$ nm, in close agreement with the total amount of deposited material (10 unit cells). This diffractogram can be completely indexed with an out-of-plane lattice parameter $d_{\perp} = 1{\cdot}2844 \pm 0{\cdot}0005$ nm, close to the calculated value ($d_{(100)} = 1{\cdot}2864$ nm) reported for the $LaTiO_{3{\cdot}5}$ unit cell.[8] Hence the main part of the film is *a*-axis oriented, with the ordered oxygen layers lying parallel to the substrate surface. A cross-sectional TEM study performed along the [$\bar{1}$10] and [001] directions confirmed the orientation of the oxygen layers.[13] The image shown in Fig. 2, taken along the [$\bar{1}$10] direction, clearly shows the characteristic monoclinic angle of the $LaTiO_{3{\cdot}5}$ structure. The distance between the clear bright lines is 1·28 nm, corresponding to the (100) interplanar spacing. The periodicity further confirms a homogeneous film growth.

3.2 In situ study of the growth mechanism

During deposition, epitaxial growth of the film leads to well-defined RHEED streaks along [$\bar{1}$10] azimuths, [Fig. 3(a)]. No precipitates can be observed, and there is no indication of three-dimensional growth. One notices the weak twofold superstructure, in agreement with a *c*-axis that is twice that of $LaTiO_{3{\cdot}5}$. From the distance between the streaks, the in-plane lattice parameter can be derived with an accuracy of $\pm 0{\cdot}002$ Å using a peak-fitting program. Figure 3(b) shows the variation of this parameter during the growth of a film 10 unit cells thick. Surprisingly, the $d_{(001)}$ distance oscillates during growth. As the number of maxima equals the number of deposited unit cells, this phenomenon is most likely associated with the formation of each unit cell.

4 Discussion

In a previous paper, we reported a deviation of the surface structure with respect to the ideal perovskite (110) one.[3] This deviation is due to a preferential ordering of the oxygen atoms along the [001] direction, within a disordered $LaTiO_{3{\cdot}5}$ topmost layer.[13] It indicates a tendency towards a *b*-axis growth mode, i.e. with the additional oxygen planes perpendicular to the surface, [Fig. 4(a)]. However, our structural data indicate that the oxygen atoms ultimately order parallel to the substrate surface. The transition from a disordered $LaTiO_{3{\cdot}5}$ surface layer to an *a*-axis ordered $LaTiO_{3{\cdot}5}$ film takes place during growth and/or cooling. The oscillations of $d_{(001)}$ [Fig. 3(b)], suggest that this transition takes place for each deposited unit cell. As previously reported,[13] we can first assume that close to the interface, i.e. within the depth probed by the electron beam, the structure corresponds to a highly oxygenated and disordered $LaTiO_x$ perovskite having a lattice parameter larger than that of bulk $LaTiO_{3{\cdot}5}$. From the bulk La–Ti–O phase diagram, we know that the smallest periodic distance between oxygen layers is 1·28 nm, which corresponds to four $LaTiO_x$ atomic layers. Hence, the ordering between oxygen layers can occur when at least four layers have been deposited. Therefore the in-plane lattice parameter increases until four layers have been reached. The subsequent decrease corresponds then to the diffusion of the oxygen atoms towards their final ordered positions, leading to a relaxation of the lattice spacing [Fig. 4(b)]. The diffusion takes place within at most two perovskite slabs, which is in agreement with the TEM analysis.[13] This analysis revealed that the first oxygen after the interface is two $LaTiO_x$ atomic layers away from the interface. This diffusion is probably driven by the epitaxial constraints coming up from the substrate. The ordering of oxygen atoms into planes parallel to the surface leads to a small lattice mismatch (0·47 and −0·12%) whereas inserting oxygen planes perpendicular to (110) would lead to a much stronger lattice mismatch.

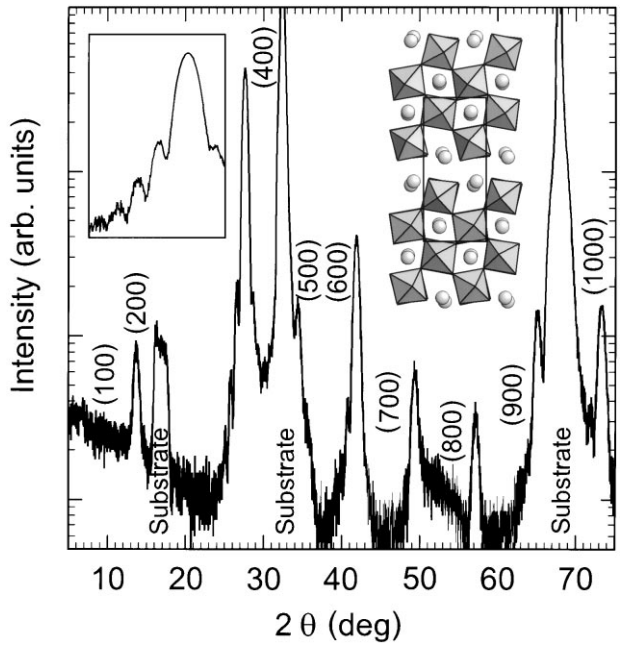

Fig. 1. $\theta - 2\theta$ X-ray diffractogram of a $LaTiO_{3{\cdot}5}$ film grown on STO. The inset shows the low-angle finite-size oscillations around the (400) reflection. Also shown is a projection on the (a, b)-plane of the crystal structure of $LaTiO_{3{\cdot}5}$. The *a*-axis is drawn vertically.

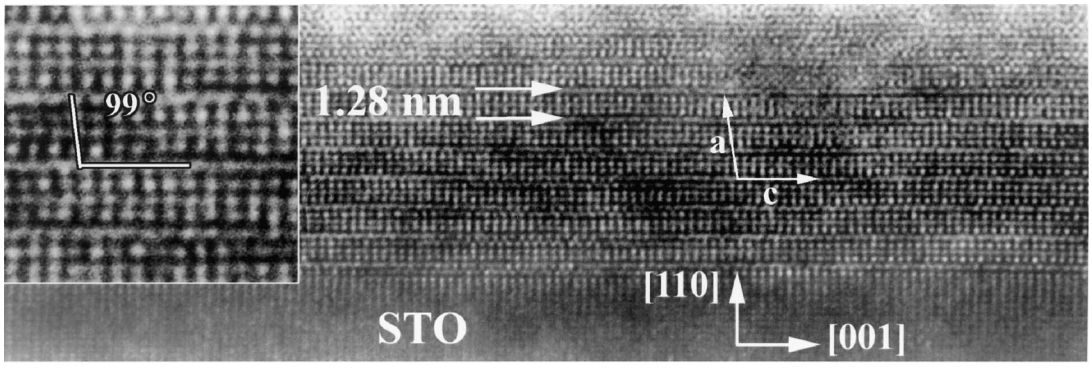

Fig. 2. $[110]_{STO}$ cross-section HRTEM image of the $LaTiO_{3.5}$ film grown on STO. The film exhibits characteristic (100) lattice fringes parallel to the interface, indicating homogeneous growth. The monoclinic angle of the $LaTiO_{3.5}$ phase can be measured from the inset. Reprinted from Ref. 13.

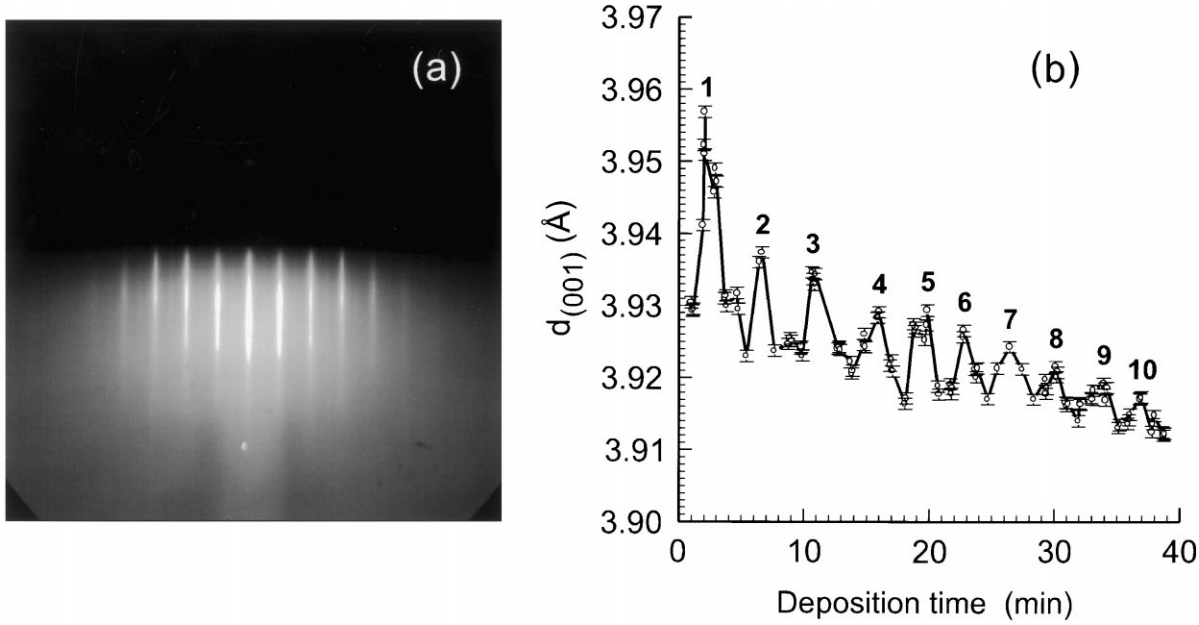

Fig. 3. (a) RHEED pattern observed during growth along $[\bar{1}10]$ azimuth. (b) Evolution of the in-plane lattice parameter measured along $[\bar{1}10]$ azimuth for a $LaTiO_{3.5}$ film grown on STO.

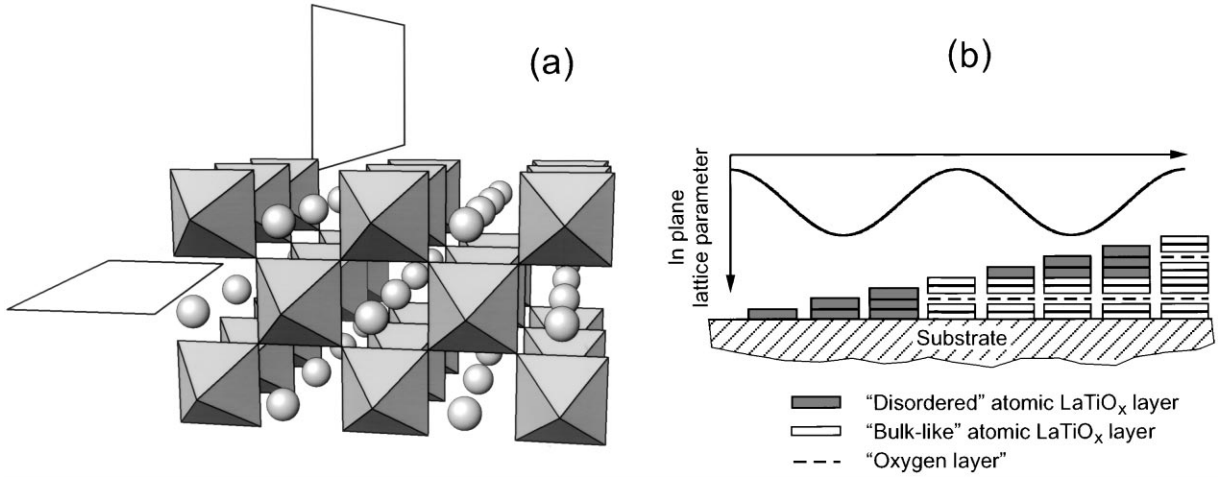

Fig. 4. Schematic for the growth mode hypothesis. (a) Two equivalent (110) planes are drawn with respect to the simple perovskite structure. The horizontal plane can be associated with the substrate surface and is the one desired for the oxygen layers. The vertical one is parallel to $[001]_{STO}$. (b) Illustration of the growth mechanism. The shaded rectangles correspond to layers with a higher in-plane lattice parameter.

5 Conclusion

We have grown epitaxial *a*-axis single crystal $LaTiO_{3.5}$ thin films on STO(110) substrates with excellent structural properties. The growth mechanism of these films is driven by the diffusion of oxygen into planes parallel to the growth surface. Their ordering parallel to the growth surface is probably due to an excellent epitaxial relationship with small lattice mismatch.

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