Microstructural investigation of strontium titanate films grown by interval pulsed laser deposition

YY Tse¹, SRC McMitchell², TJ Jackson², IP Jones¹ and AGenc³

¹ School of Metallurgy and Materials, University of Birmingham, Birmingham, B15 2TT, UK
² School of Electronic, Electrical and Computer Engineering, University of Birmingham, Birmingham, B15 2TT, UK.
³ Department of Materials Science and Engineering, Ohio State University, 2041 College Rd, Columbus, OH 43210

E-mail: y.y.tse@bham.ac.uk

Abstract. Strontium titanate (SrTiO₃) films were deposited on (001) magnesium oxide (MgO) substrates by pulsed laser interval deposition (PLID). The growth modes of the films were monitored by in-situ reflection high-energy electron diffraction (RHEED). The microstructures were investigated by transmission electron microscopy (TEM). It has been shown that PLID can enhance the two dimensional (2D) growth of this system, which has the large lattice misfit of 7.9%. The addition of a mono TiO₂ buffer layer to the MgO substrate surface further improved the 2D growth mode. TEM results revealed that the films grown in 2D mode with large lattice mismatch were dominated by antiphase boundaries (APBs) and holes. All the holes were connected by antiphase boundaries. The holes were rectangular in shape, with facets along the [100] and [010] directions, and they ran through the whole film thickness. Threading and misfit dislocations have also been identified as growth defects in the films grown with and without a TiO₂ buffer layer. However, the density of defects varies with growth mode.

1. Introduction
SrTiO₃ (STO) is an alkaline earth titanate which is widely used in microelectronics. The unique dielectric properties of STO thin films at low temperatures are important in microwave applications [1]. Conventional pulsed laser deposition (PLD) is popular for growing complex oxide films because it can maintain good stoichiometric transfer of materials from target to substrate [2]. However, the high density of defects formed during deposition of STO thin films leads to a higher dielectric loss in thin films than in bulk material - in the order of about 100 [3]. Therefore, it is of technical importance to grow the film with fewer defects. Forced layer by layer growth will give an atomically flat interface and reduce the density of the growth defects of the films. The novel pulsed laser interval deposition (PLID) technique was introduced to achieve “true” layer by layer growth in homo- and closely matched hetero-epitaxy [4, 5]. In PLD, laser pulses at a fixed rate were used during deposition, but in PLID, rapid bursts of laser pulses were used, each burst being sufficient to deposit a monolayer of material. The growth mode was intensively investigated by in-situ reflection high-energy electron diffraction (RHEED) and layer by layer growth was confirmed via the temporal evolution of the RHEED intensity [4, 5]. The purpose of this work was to study the microstructure features of heteroepitaxial films with large misfit (∼ 7.9%) by PLID.

2. Experiment
STO thin films with nominal thickness of 40 nm, with and without a TiO₂ buffer layer, were deposited on (001) MgO by PLID equipped with in-situ RHEED. Deposition parameters and detailed studies of
the RHEED are described elsewhere [6]. Plan view and cross section TEM samples were prepared by tripod polishing to electron transparency. TEM and high resolution TEM were carried out using a Tecnai F20 microscope operated at 200kV. High resolution scanning TEM (HRSTEM) work was carried out using a probe corrected FEI Titan operated at 300kV with a probe size of about 0.1 nm. The high angle annular dark field (HAADF) collection angle is ranged from 46 – 325 mrad. DigitalMicrograph was used to analyse the HRSTEM images.

3. Results and Discussion

The evolution of the RHEED intensity during growth was used to confirm the layer by layer growth mode of the films [6]. The purpose of growing the film with a TiO$_2$ buffer layer is to wet the MgO surface, ensuring that the initial layer deposited is TiO$_2$ instead of SrO, which has a higher interfacial energy [7]. The addition of TiO$_2$ buffer layer will further promote the layer by layer growth mode. A film without a TiO$_2$ layer was grown to compare the growth modes and subsequent microstructures. Figure 1 shows a pair of cross-sectional two beam bright field images taken with (a) g = -200 and (b) g = 002 of an STO film grown without a TiO$_2$ buffer layer. The film was of uniform thickness with a few threading dislocations (marked by the black arrows in figure 1a) when compared to films grown by standard PLD [8]. APBs were observed and indicated by the white arrows in figure 1b.

![Figure 1](image)

**Figure 1** Cross-sectional two beam bright field images of film without TiO$_2$ buffer layer taken with (a) g = -200 and (b) g = 002. The APBs are marked by white arrows and threading dislocations are marked by black arrows.

Figure 2a shows a HRSTEM HAADF image taken with B = [001] showing the interface and the inset is the FFT filtered image of the region marked by square. Figure 2b shows the intensity profile of the Sr, Ti and Mg atoms from the film region to the substrate. The HAADF image of the interface was not clear due to sample drift, specimen thickness and the different scattering power of the STO and MgO. With the aid of the intensity profile, it was possible to determine the initial atomic layer of the film in specific regions. The intensity drop from the Sr to a Ti atom was estimated using 10 different areas from three different HRSTEM images, and is about 25 ± 5%. As shown in figure 2b, the diagonal spacing between the Sr and Ti atoms is 0.26 nm. Assuming the relative intensity drop near the interface was similar to those in the film region, it was expected to see the Ti peak at the position marked by the dotted line with intensity 64 ± 4 a.u. (the intensity of the corresponding Sr atom from the intensity profile is 85 a.u.). However, there is no peak in that particular position, which indicates that the first atomic layer above the MgO substrate was Sr. Albeit TiO$_2$ is energetically favourable to form during deposition, there exists some regions covered by SrO as the initial deposited atomic layer. This result was consistent with the AFM observation on a four monolayer STO film on MgO, which showed the presence of SrO inclusions [8]. Figure 3 shows the intensity profile of Sr, Ti and Mg obtained from the line drawn across the interface indicated in the inset HAADF image. Most of the interfacial areas were covered by TiO$_2$ as the initial atomic layer since TiO$_2$ is energetically favourable to form on MgO substrate. The variation of Mg-Mg distance close to the interface might be due to the large misfit strain and the atomic steps on the surface of the MgO. From the RHEED result [6], the
growth mode of the film without a TiO$_2$ buffer layer was not entirely two dimensional: the growth mode changed to three dimensional in the later stages of deposition. The existence of SrO inclusions may cause the nucleation of three dimensional growth in the later part of the deposition.

**Figure 2** (a) Cross-sectional HRSTEM HAADF image taken with B = [001] showing the SrO as the termination layer of a film grown without a TiO$_2$ buffer layer. The inset is the FFT filtered image of the area marked by the square. (b) The intensity line profile from the film to the substrate and the line position is illustrated in figure 2a.

Therefore, to promote the 2D growth mode further, an artificial TiO$_2$ buffer layer was deposited prior to the STO film to wet the MgO surface. Figure 4a shows a cross-sectional bright field image taken with $g = 200$. More APBs were observed in the STO film with a buffer layer and the film has even less threading dislocations than the film without a buffer layer. Figure 4b shows the HRTEM of the interface of the STO film with a TiO$_2$ buffer layer. The interface is sharp since there is no second phase or amorphous layer but the roughness of 0.5 to 2 nm was observed (figure 4b). The steps on the MgO surface are highlighted by the dotted line in figure 4b. It is interesting to note that the atomic column contrast was good on both STO and MgO sides but became unclear at the interface. This may be due to either the roughness of the MgO substrate in the direction parallel to the electron beam or the fact that the interface was strained. For similar reasons, there is no clear enough HRSTEM HAADF image to carry out the intensity profile analysis for the initial atomic layer of this film with a TiO$_2$ buffer layer. More work will be continued to verify that issue. As indicated by the arrows in figure 4a, there is a gap running from the substrate to the top of the film was observed. To confirm the existence of the holes, a plan view TEM sample was prepared. Figure 5 shows the holes were of rectangular/square shape and the edges of the hole are on {100} planes. The holes were connected by the APBs. A tilting series suggests that most of the APBs can be characterised with displacement vector $R = 1/2[010]$ or $1/2[100]$. When ordered planar faults were transposed from one set to another set of {100} plane, the interface would form a zig-zag boundary as shown in the inset to figure 5. RHEED results suggested the film was forced in a layer by layer growth mode through its entire thickness by PLID despite the large mismatch (~7.9%). The microstructure revealed by TEM showing a high density of APBs, holes and low density of threading dislocations suggests that a high level of
strain was developed during deposition. Therefore, fracture caused by strain may occur in <010> directions during cooling the film from 850°C to room temperature after deposition. High resolution HAADF STEM taken in plan view shows the fracture might occur at the junction of two or three 1/2[010] APBs where the APBs energy is the highest.

![Image of TEM bright field image of STO film with TiO$_2$ buffer layer taken at g = 200. The hole is marked by white arrows and the threading dislocation is marked by black arrow.](image1)

![Image of HRTEM of STO and MgO interface. The steps on the MgO substrate are highlighted by the dotted line.](image2)

**Figure 4** (a) TEM bright field image of STO film with TiO$_2$ buffer layer taken at g = 200. The hole is marked by white arrows and the threading dislocation is marked by black arrow. (b) HRTEM of STO and MgO interface. The steps on the MgO substrate are highlighted by the dotted line.

**Figure 5** Two beam bright field plan view image of STO film with TiO$_2$ buffer layer. Image taken with g = 110 and showing holes are connected by APBs. Inset is a zoom in of the zig-zag APBs.

4. Conclusions
There exist small regions of SrO as the initial atomic layer in the STO film without a TiO$_2$ buffer which may nucleate three dimensional growth. Instead of forming a large number of threading dislocations, the film grown in layer by layer mode has a tremendous amount of 1/2[010] or 1/2[100] APBs and holes.

Acknowledgement
The authors thank Professor Hamish Fraser (Ohio State University) for invitation to use Titan for the HRSTEM work.

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