Microstructure of Homoepitaxial SrTiO$_3$ Films Deposited by Laser Ablation

Y.Y. Tse$^1$, T.J. Jackson$^2$, Y. Koutsonas$^2$, G. Passerieux$^1$ and I.P. Jones$^1$

School of Engineering, 1) Department of Metallurgy and Materials, 2) Department of Electronic, Electrical and Computer Engineering, The University of Birmingham, Edgbaston, Birmingham B15 2TT, UK.

Email address: y.y.tse@bham.ac.uk

Abstract: Homoepitaxial strontium titanate thin films have been grown by pulsed laser deposition on (001) SrTiO$_3$ (STO) substrates with pulse rates ranging from 0.15 Hz to 100 Hz. The microstructure of the as-deposited films has been characterised by cross-sectional transmission electron microscopy. It is found that the growth mode and microstructure of the films are strongly influenced by the intervals between the laser pulses. Films have homogeneous microstructure under a critical thickness, above which the film breaks into tooth-like columns. The growth is unstable against the formation of low angle boundaries which result in the formation of grains elongated in the direction of film growth. These become tooth-like structures and the size of the tooth depends on the pulse rate and the growth time. The diffusion of point defects in films grown over a long time can lead instead to the development of elongated vacancy clusters directed normal to the film-vacuum interface. All films grow with a high density of point defects which may be related to deviation from the stoichiometry of the ceramic ablation target. Microanalysis suggests that there is strontium loss in the film, which causes defect formation inside the STO films.

1. Introduction

SrTiO$_3$ and BaxSr$_{1-x}$TiO$_3$ are widely studied as materials with high permittivity and low dielectric loss and suitable for incorporation in tuneable microwave devices. However, the dielectric losses of films generally far exceed those found in bulk single crystals. This difference is widely attributed to oxygen non-stoichiometry or to some microstructural properties. For example, cross-sectional TEM studies of heteroepitaxial SrTiO$_3$ and BaxSrTiO$_3$ films grown by pulsed laser deposition (PLD) commonly show columnar contrast [1, 2]. It has been suggested that this microstructure arises, for example, from antdomain boundaries between regions of the film growing on adjacent terraces on a stepped substrate surface. Alternatively it may be associated with a diffusion limited island growth mode. Analysis of the dielectric properties at microwave frequencies using a phenomenological model [3] has suggested that there is a large distribution of electric fields within the materials, perhaps due to “charged defects” of some nature. In trying to correlate particular defects with the dielectric response, it is useful to determine which defects are intrinsic to the growth of these materials as thin films i.e. to growth kinetics, and which are related to the lattice and chemical mismatch with the substrate. Homoepitaxial growth offers an opportunity to separate these influences and thus lead to a better understanding of heteroepitaxy. PLD is a successful method for complex oxide film preparation due to the advantage of congruent ablation and the possibility to use relatively high oxygen pressure. The objective of this
work was to identify the microstructures present in films grown with laser pulse rates in the range $10^{-1} - 10^2$ Hz.

2. Experimental
The (001) SrTiO$_3$ substrates were cleaned ultrasonically with acetone and methanol prior to gluing to the substrate heater with silver dag. A KrF excimer laser producing laser radiation with a wavelength of 248 nm and a pulse duration of 20 ns was focussed to a spot size of 8mm$^2$ on the target, producing an energy density of 1.5 J/cm$^2$. The ceramic target, 99.99% pure, was rotated throughout the deposition to spread the laser-induced damage. The target-to-substrate distance was fixed at 6.5 cm. The films were deposited at 750°C in oxygen flowing through the deposition chamber at a rate of 10 sccm and at a pressure of 0.4 mbar. After growth, oxygen was admitted to the chamber up to a static pressure of 400 mbar and the substrate held at 650°C for one hour before free cooling to room temperature. The films were grown at constant thickness of 5000 pulses and laser frequencies of 0.15, 1 and 100 Hz.

TEM cross-sections were prepared using the tripod polishing technique [4]. Pure mechanical polishing was chosen over ion milling to avoid sputter etching of the film and thereby improve the accuracy of chemical analysis. TEM studies were carried out on a Tecnai F20 operating at 200 kV and equipped with Oxford instruments EDX.

3. Results and Discussion

| Sample | Low Magnification general view | Thickness (nm) ± 10 nm |
|--------|--------------------------------|------------------------|
| 0.15 Hz| ![Tooth-like column Matrix](image) | 469                    |
| 1 Hz   | ![Tooth-like column Matrix](image) | 427                    |
| 100 Hz | ![Tooth-like column Matrix](image) | 302                    |

Table 1 Summary of homoepitaxial films in this study. All films were deposited at 5000 pulses with substrate temperature 750°C except where indicated.

Table 1 lists the low magnification cross-sectional TEM images of films grown at different pulse rates. All the deposition parameters are the same except those specified. In the film grown at 0.15 Hz, there are clear tooth-like columns as shown in cross-section. The roots of the tooth-like columns originate from or close to the interface. The diameter of each tooth-like column is about 130 nm to 170 nm. The
columns are subgrains of the same phase bounded by low angle boundaries [5]. As shown in figure 1 (a), there are elongated inclusions inside the matrix regions which are not found at faster pulse rates. They formed during the growth of the film and most of them are at the interface. Stereomicroscopy shows that these defects appear through the thickness of the TEM foil and are not defects on the surface of the sample induced during sample preparation. A high resolution image taken along [010] of the film substrate interface for the sample grown at 0.15 Hz is shown in Figure 2. There is more contrast visible in the film than the substrate. The lattices of the film and substrate are clearly coherent. The (001) interplanar spacing in the substrate deduced from the high resolution image is roughly 0.390 nm, which agrees with the bulk value. However, at such high resolution, the images do not reveal the overall natures of the films. The composition analyses show that chemical compositions of the substrate and film are close to stoichiometry, but that the defects are Sr deficient. Figure 1(b) shows a scan across one of the elongated features. A slight drop in Sr concentration was detected.

EDX results also show there is Sr deficiency at the column boundaries.

Film grown at 1 Hz shows features similar to the columns observed in the 0.15Hz film (see table 1). A high resolution image again shows a coherent interface without misfit dislocations is seen but there is again increased contrast in the film compared with the substrate. No additional spots were found in the SAD patterns, indicating good single crystallinity. There is no sign in the film grown at 1 Hz of the elongated features observed in the matrix regions of the 0.15 Hz sample. The column size of the film grown at 1 Hz is reduced to 80 nm. Compositional analysis showed that the film overall is about as stoichiometric as the films grown at 0.15 Hz.

Low magnification cross-sections of the film grown at 100 Hz is also shown in table 1. In this film, a homogeneous layer was grown until a thickness of approximately 211 nm. A film which grown at the same condition but approximately half of the thickness, i.e. with just 2500 pulses, is homogeneous throughout its thickness. This suggests that the layer by layer growth is breaking down after a critical thickness. The diameter of the columnar features (~ 45 nm) at the surface was smaller than in the case of the 1 Hz and 0.15 Hz films.

Figure 1 (a) Elongated defects found in the matrix of the film grown at 0.15Hz. (b) Composition scan across one of the elongated features.

The columnar structures can be seen in films grown with laser pulse rates from 0.15 Hz to 100 Hz. The contrast in the TEM images of the columns appears to arise from low angle boundaries between the columns. They may be regarded in some sense as growth islands, growing through thermally activated processes, probably including diffusion from the early stages of film growth in the majority of cases.

The elongated features in the 0.15 Hz films occur most frequently near the substrate-film interface. Above the interface they appear randomly distributed through the thickness of the film with an average spacing of around 50 nm. They are not seen in the 1 Hz or 100 Hz films. This suggests that a
total film deposition time of between approximately one and a half hours and 9 hours is required for them to form. From this estimate of the cation diffusivity, of between $5 \times 10^{-19} \text{ m}^2\text{s}^{-1}$ and $8 \times 10^{-20} \text{ m}^2\text{s}^{-1}$, may be obtained. This is consistent with the cation diffusion data of Freer [6] and Lippmaa[7].

Figure 2 High resolution image of film grown at 0.15 Hz taken along [010], showing the coherence of film and substrate.

We believe that both the columns and the elongated defects emanate from diffusion processes and are probably connected with Sr vacancies, we know that Sr is lost preferentially from the target [5]. SrTiO$_3$ is a line compound. The Sr vacancies (or Ti + O interstitials) wish to precipitate somewhere. We believe that amorphous TiO$_2$ deposits either form between columns or as elongated defects, depending on pulse rate and time.

References
[1] B.H. Park, Y. Gim, Y. Fan, Q. X. Jia and P. Lu, Applied Physics Letters, 77, 2587 (2000).
[2] C.L. Chen, J. Shen, S.Y. Chen, G.P. Luo, C.W. Chu, F.A. Miranda, F.W. van Keuls, J.C. Jiang, E.I. Meletis and H.Y. Chang, Applied Physics Letters, 78, 652 (2001).
[3] O.G. Vendik, S.P. Zubko and M.A. Nikol’ski, Journal of Applied Physics, 92, 7448 (2002).
[4] J. Ayache and P. H. Albarède, Ultramicroscopy, 60, 195 (1995).
[5] Y.Y. Tse, Y. Koutsonas, T.J. Jackson, G. Passerieux and I.P. Jones, submitted to Thin Solid Films (2005).
[6] R. Freer, Journal of Materials Science, 15, 803 (1980).
[7] M. Lippmaa, N. Nakagawa, S. Ohashi and H. Koinamu, Applied Physics Letters, 76, 2439 (2000).