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Line defects, planar defects and voids in $SrTiO_3$ films grown on MgO by pulsed laser and pulsed laser interval deposition

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ABSTRACT

Two and three dimensional growth of $SrTiO_3$ films on (001) MgO substrate was achieved by pulsed laser interval and pulsed laser deposition respectively. The growth mode was monitored by in-situ reflection high energy electron diffraction. Interval deposition forces layer-by-layer growth of materials even with such a large lattice misfit (~7.9%). A titanium dioxide buffer monolayer was deposited to allow the film to wet the substrate to encourage two dimensional growth of the strontium titanate. A variety of defects was investigated using transmission electron microscopy and high resolution scanning transmission electron microscopy. Misfit dislocations, steps at the interface, Ti-rich defects and regularly shaped nano-holes connected by anti-phase boundaries were found to be the dominant defects in these films grown layer by layer. The edges of the nano-holes were mainly along [010] and [100] for a [001] growth direction. The large strain between the two crystal systems with large lattice mismatch leads to in-plane tensile stress during the layer-by-layer growth. The stress is relieved in part by the holes. The films with a three dimensional growth mode possess a uniform surface with dislocations as the dominant defects. The individual densities of the various defects, including a Ti-rich phase and misfit and threading dislocations, are determined by the kinetics of the deposition method.

1. Introduction

Thin films of oxide materials, including strontium titanate (STO) and related perovskites, are being used in an increasing number of applications due to their catalytic, electronic and ferroelectric properties. The growth mode and defect structure of ferroelectric films greatly affect their dielectric tunability and loss [1–3]. In films grown in a three-dimensional (3D) mode, even including in some homoepitaxial systems, defects such as low angle grain boundaries, columnar grains, misfit and threading dislocations are common, depending on the growth parameters [1,2]. The existence of low angle grain boundaries and a high density of threading dislocations have been reported to be associated with reduced voltage-tunability of the dielectric properties [1,2,4]. Therefore, it is technically important to grow the films with fewer such defects.

Pulsed laser deposition (PLD) has been widely used for preparing thin films of complex oxide materials [5]. The conventional PLD method, in which the laser is fired with pulses at a fixed repetition rate of the order of 2–10 Hz, often produces thin films via a three dimensional growth mode [2,6]. The growth mode is due to lattice mismatch and/or limited mobility of adatoms on the substrate. For microwave applications, MgO (001) single crystal substrate has an excellent dielectric constant $\varepsilon<9.5$ and a loss tangent, tan $\delta = 3.3\times10^{-7}$ [7]. These attributes make MgO preferable to other commonly used substrates e.g. $LaAlO_3$ and $SrTiO_3$. However, the large lattice mismatch between the ferroelectric films and MgO, e.g. $Ba_{0.5}Sr_{0.5}TiO_3$ (BSTO) on MgO (001) (~6.5%) and STO on MgO (001) (~7.9%), makes growing high quality two dimensional films difficult. A true layer by layer growth has been obtained in the homoepitaxial system $SrTiO_3$ on $SrTiO_3$ by using pulsed laser interval deposition (PLID) with in-situ reflection high energy electron diffraction (RHEED) to guide and monitor the growth mode [8]. PLID was quite quickly extended to closely-matched heteroepitaxy [8] but only recently to the growth of films with large lattice mismatch with the substrate [9]. Relatively little work has been performed on the microstructural characterisation of films grown by PLID.

PLD is a thermodynamically non-equilibrium process in which all species land on the substrate within a growth pulse of a few microseconds in duration. Second phase non-stoichiometric defects can be formed during growth [10]. The most frequently observed metastable phases in the perovskite ABO_3 structure are Ruddlesden-

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Popper compounds (A-site rich) [11]. B-site rich phases, e.g. TiO_2, may also form via non-equilibrium processes leading to crystallographically sheared double layers which are closely related to dislocation loops, stacking faults and misfit dislocations [12,13].

The aim of this work was to manipulate the growth mode of a system with large lattice mismatch (STO on MgO(001)) using buffer layers and the PLID method, in order to understand the relationship between growth mode and microstructure. The microstructural study included analysis of plan view and cross sectional images taken in a transmission electron microscope (TEM), of data taken in a high resolution scanning transmission electron microscope (HRSTEM) and from ex-situ atomic force microscope (AFM) images. It will be shown that the relaxation of the large lattice mismatch between STO and MgO occurs through several types of defect in 2D growth mode films: misfit dislocations, antiphase boundaries (APBs) and nano-holes, whilst in 3D growth mode films, the dominant defects are misfit and threading dislocations.

2. Experimental details

Four STO films with thickness 40 nm were deposited on (001) MgO substrates using a KrF excimer laser with a wavelength of 248 nm. The substrate was held at a temperature of 850 °C and 45 mm away from the targets (99.99% pure stoichiometric $SrTiO_3$ and TiO_2). Two of the films were grown by standard PLD, with and without an atomic thickness mono-layer of TiO_2 as a buffer layer. Another two films also with and without a TiO_2 buffer layer, were grown by PLID. Different laser fluences of 4 J/cm^2 and 3 J/cm^2 were used for depositing the $SrTiO_3$ and TiO_2 layers respectively. The optimised deposition parameters and the method for calibrating the number of pulses required for one monolayer were as described previously [14]. For standard PLD, a continuous 5 Hz laser pulse repetition rate was used. For PLID, the laser repetition rate was set to 60 Hz during the burst of pulses which allowed the deposition of one monolayer. Sufficient time was given for the relaxation and crystallisation of the deposited material after each burst — about 15 s [14,15]. The growth modes of all the films were monitored using the in-situ RHEED system. Plan view and cross sectional TEM samples were prepared by tripod polishing to electron transparency to avoid any ion contamination as might occur if prepared by Ar or Ga ion milling. Conventional TEM investigations were carried out using a Tecnai F20 operated at 200 kV. High resolution scanning TEM (HRSTEM) work was carried out using a probe-corrected FEI Titan operated at 300 kV with a probe size of about 0.1 nm. The high angle annular dark field (HAADF) collection angle ranged from 46 to 325 mrad. DigitalMicrograph was used to analyse the HRSTEM images. An MultiMode™ SPM Atomic Force Microscope (AFM) with silicon probe in tapping mode was used to measure the surface morphology and roughness of the films.

3. Results

Fig. 1a and b shows the RHEED intensity during the first 500 s of growth of the $SrTiO_3$ film by PLD with and without a TiO_2 buffer layer. The intensity dropped rapidly in both cases, which indicates a 3D growth mode. Fig. 1a shows a peak in intensity at the beginning of the growth of the film with the TiO_2 buffer layer as marked by the arrow. This was not an oscillation due to two dimensional growth; a shift in the position of the specular RHEED peak was observed at a time corresponding to this peak in intensity. In fact, this was due to the STO specular reflection increasing as the MgO/TiO_2 specular reflection died out which shows the buffer layer allowed STO to wet the surface completely and lead to a smoother surface in the initial stages of growth — an improved growth regime.

Fig. 2 shows the variation of the specular RHEED intensity of the films grown by PLID with TiO_2. Fig. 2a–d shows the drop-and-recovery cycle during deposition of the whole 100 monolayers. This is evidence that the $SrTiO_3$ film grown by PLID on a TiO_2 monolayer follows LBL growth throughout the whole deposition [9]. The drop-and-recovery cycle of the intensity for the film grown without a TiO_2 buffer layer as shown in Fig. 3 becomes lost in the noise

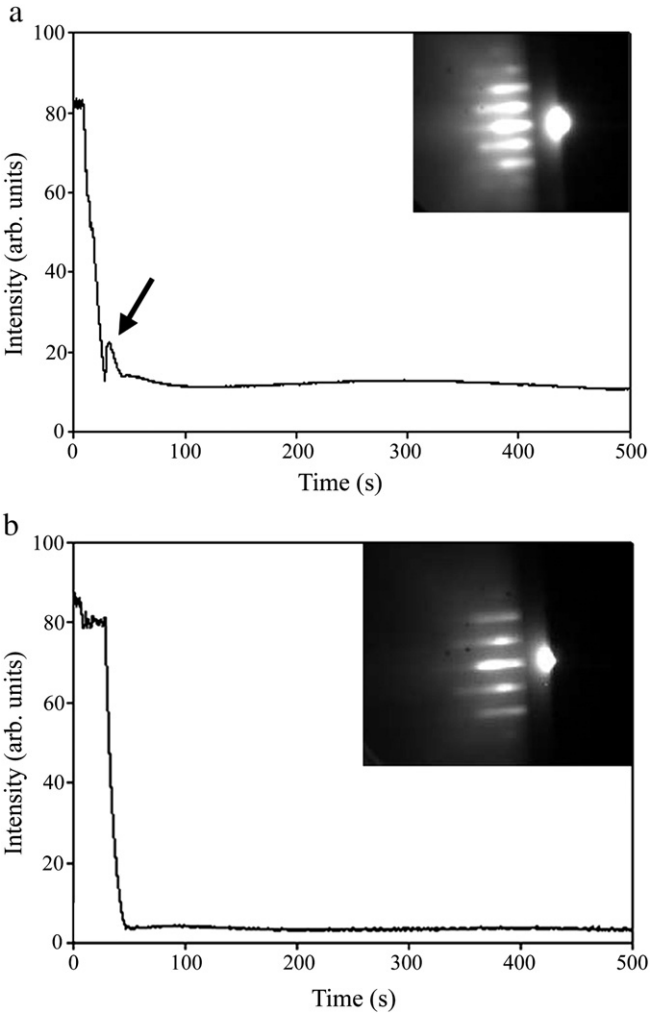

Fig. 1. Specular RHEED intensity for the first 500 s of the PLD deposition process (a) with a TiO_2 buffer layer, (b) without a TiO_2 buffer layer. The insets show the diffraction pattern with the electron beam along [100] after standard PLD of a 40 nm thick film.

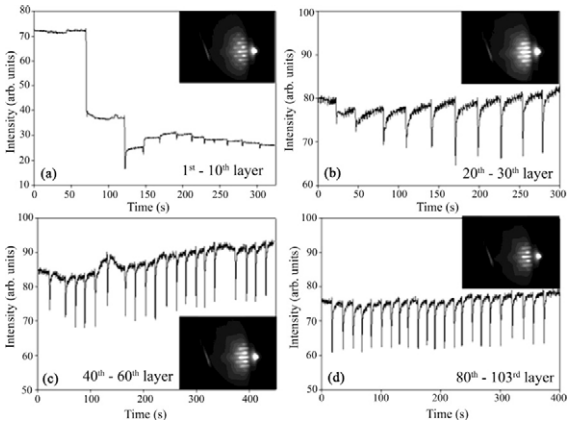

Fig. 2. Specular RHEED intensity for STO grown by PLID with a TiO_2 buffer layer, (a) first 10 layers, (b) 20th to 30th layers, (c) 40th to 60th layers and (d) the last 23 layers. The insets show the diffraction pattern taken with the electron beam along the [100] direction after PLID of a 40 nm thick film.