	Experiment title: Reciprocal space mapping of strain and tilt in epitaxial anatase on $SrTiO_3$	**Experiment number**: 28-01 969
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Names and affiliations of applicants (* indicates experimentalists):

A. Regoutz[1]*, R.G. Egdell[1]*, K.H.L. Zhang[1], R.A. Cowley[2] and C.R. Poll[3]*

1. Department of Chemistry, University of Oxford, Inorganic Chemistry Laboratory, South Parks Road, Oxford OX1 3QR, UK.
2. Department of Physics, University of Oxford, Clarendon Laboratory, Parks Road, Oxford OX1 3PU, UK.
3. Department of Materials, Imperial College London, Exhibition Road, London, SW7 2AZ, UK.

Introduction

TiO_2 has two important tetragonal phases: rutile with a = 4.594 Å, c = 2.959 Å, z = 2; and anatase with a = 3.785 Å, c = 9.514 Å, z = 4. Anatase has an indirect bandgap of 3.20 eV, somewhat bigger than the direct gap of 3.06 eV found for rutile. Anatase has emerged as one of the most promising of all photocatalytic materials, with the proprietary formulation Degussa P25 (a high area mixture of anatase and rutile) widely regarded as a benchmark standard against which to appraise other photocatalysts[1-3]. The anatase polymorph of TiO_2 is not thermodynamically stable at room temperature but can be prepared by sol gel routes as a high area powder metastable up to about 600 °C. Fundamental studies of anatase surfaces are limited by the scarcity and limited stability of anatase single crystals. It has emerged however that anatase can be grown epitaxially on cubic $SrTiO_3$(001) with a=3.905 Å by techniques such as molecular beam epitaxy owing to the relatively small mismatch of -3.1% between the a parameters[4,5]. We have recently shown that highly ordered epitaxial anatase(001) ultra-thin films can be grown by a much simpler simple dip coating process involving a titanium isopropoxide precursor, followed by annealing at temperatures up to 1000 °C. Here we make a detailed study of these epitaxial films by high resolution X-ray diffraction. In particular we have investigated the impact of the very different coefficients of thermal expansion for anatase and $SrTiO_3$ by meaurements over a range of temperatures up to 600 °C.

Experimental

Samples were prepared by a dip coating method. Titanium (IV) isopropoxide was dissolved in isopropanol to give 25 cm^3 of a solution with 0.33 M Ti concentration, which was acidified using HNO_3 (HNO_3/Ti molar ratio 0.15). The resulting solution was used to dip coat $SrTiO_3$(001) substrates in a 25 cm^3 wide neck flask. The substrates were cleaned by rinsing in isopropanol. After immersion, substrates were withdrawn from the alkoxide solution using a motor drive at a pulling rate of 3.5 mm/min. The wet substrates were immediately placed in flowing N_2 gas saturated with H_2O at room temperature, so that the alkoxide was hydrolysed on the $SrTiO_3$(001) surface. The amorphous film products of the hydrolysis were calcined for 4 hours at either 700 °C or 1000 °C to form epitaxial films of anatase TiO_2. Diffraction experiments were performed on three samples (2 and 4 dip samples pre annealed at 1000 °C and a 4 dip sample annealed at 700 °C) on the beamline XMaS/BM28 using a photon energy of 15 keV, corresponding to a wavelength $\lambda = 0.8266$ Å. The samples were mounted directly in air within a furnace capable of reaching temperatures up to 600 °C. The scattered photons were detected with a Pilatus 300K two dimensional (2D) detector, here effectively operated as a point detector by integrating counts in the central group of pixels. The $SrTiO_3$ substrate was aligned using the (002) and (012) reflections and it was verified that the [010] direction of the anatase epilayer lay in the same plane as that for the substrate by scanning through the [013] epilayer reflection along the [100] direction in reciprocal space. Diffraction data are presented in terms of reciprocal lattice units of the substrate.

Results and discussion

The (004) reflection of anatase appears about midway between the (001) and (002) reflections of the $SrTiO_3$ substrate. The much weaker (008) specular reflection was also located. The mosaic spread for three of the samples were investigated by scanning through the (004) and (008) epilayer reflections along the [100] direction in reciprocal space. The full widths at half maximum height $\Delta Q[100]$ in these transverse scans decreased slightly from 0.043 reciprocal lattice units for a 4-dip 700 °C sample to 0.037 reciprocal lattice units for 2- and 4-dip samples annealed at 1000 °C. The full widths at half maximum height were found to be twice as large in the scan through the (008) peak so that the ratio $\Delta Q[100]/Q[001]$ remains roughly constant, where Q[001] is the longitudinal wavevector transfer. This shows that the broad width of the peaks arises mainly through mosaic spread rather than domain size effects Given that the wavevector transfer for the (004) peak is 1.64 these results suggest a mosaic spread of $\tan^{-1}(\Delta Q[100]/Q[001])$ i.e. 1.5° for the 4-dip sample annealed at 700 °C and a slightly smaller value of 1.3° for the 2- and 4- dip samples annealed at 1000 °C. Scans through the (004) reflection along the [001] direction (figure 1) showed that broadening for the two-dip sample annealed at 1000 °C was greater than for the 4-dip sample. Moreover, well defined Pendelosung fringes were observed, suggesting excellent thickness uniformity in the epilayers. From the peak broadening and separations between the fringes it was possible to estimate film thicknesses of 6.6 nm and 11.2 nm for the 2-dip and 4-dip samples respectively, in agreement with ellipsometric measurements.

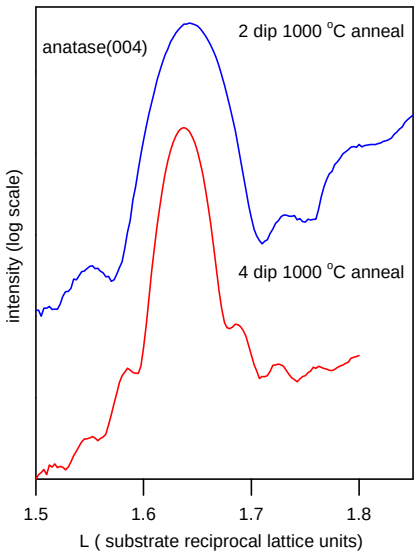

Figure 1.
The anatase (004) reflection for two thin films on $SrTiO_3$(001) presented on a logarithmic scale. Note the appearance of well-defiined Pendelosung fringes.

The variation in the position of the (004) reflection as a function of temperature in the range up to 600 °C was studied in detail as shown in the left panel of figure 1. Somewhat surprisingly there was no variation in peak position with temparature. From the bulk coefficients of thermal expansion the *c* parameter of anatase is expected to increase by 0.33% over this temperature range[6], which should produce discernible shifts. By contrast there was a large variation in the in-plane *a* parameter as gauged by shifts in the position of the (013) reflection in scans along the [010] direction in reciprocal space. In fact the shifts evident in the right hand panel of figure 2 are indicative of a 1.27 % expansion, very much greater than the 0.68% expansion expected from the bulk coefficient of thermal expansion. The key to understanding this unusual behaviour lies in recognising that the cubic $SrTiO_3$ substrate has very much higher coefficient of thermal expansion[7] which will lead to a 1.70% in-plane expansion on heating to 600 °C. Thus upon heating the anatase epilayer in placed under increasing tensile stress and expands more than expected in the in-plane direction. The tensile strain leads to a contraction in the orthogonal longitudinal direction via the Poisson effect which appears to cancel out the thermal expansion in this direction.

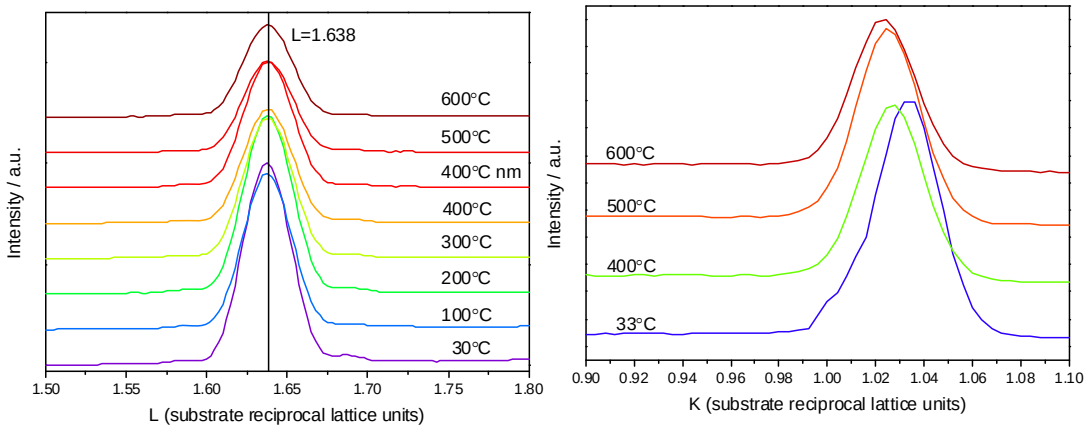

Figure 2. Left hand panel: variation in position of the (004) reflection of anatase 4-dip epitaxial film pre-annealed at 1000 °C as a function of measurement temperature. The wavevetor transfer along the [001] direction is given in reciprocal lattice units of the substrate. Right hand panel: corresponding variation of the [010] component of the (013) reflection.

Conclusions and further work

The present experiments provide valuable new insight into the influence of temperature on the strain state of anatase epilayers on $SrTiO_3$(001). The present analysis is based purely on line scans in single directions in reciprocal space. However the data that were collected will eventually allow construction of three dimensional reciprocal space isosurfaces. Software is under development which will assign each pixel on the Pilatus detector a unique (*h,k,l*) value. Using a series of Pilatus images a mesh of intensities in 3D reciprocal space can then be obtained. These can be used in turn to interpolate values on a uniformly spaced 3D grid from which scattering isosurfaces can be derived.

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