Surface Science 606 (2012) 1443–1449

Contents lists available at SciVerse ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

In-situ imaging of the nucleation and growth of epitaxial anatase $TiO_2(001)$ films on $SrTiO_3(001)$

Y. Du [a,*], D.J. Kim [b], T.C. Kaspar [b], S.E. Chamberlin [c], I. Lyubinetsky [a], S.A. Chambers [b]

[a] Environmental Molecular Sciences Laboratory, Pacific Northwest National Laboratory, Richland, WA 99352, USA
[b] Fundamental & Computational Sciences Directorate, Pacific Northwest National Laboratory, Richland, WA 99352, USA
[c] Department of Physics and Laboratory for Surface Studies, University of Wisconsin — Milwaukee, Milwaukee, WI 53211, USA

ARTICLE INFO

Article history:
Received 4 December 2011
Accepted 16 May 2012
Available online 23 May 2012

Keywords:
Anatase
TiO_2
MBE
STM
RHEED
$SrTiO_3$

ABSTRACT

The growth of TiO_2 anatase films on Nb-doped $SrTiO_3(001)$ molecular beam epitaxy has been studied in-situ by scanning tunneling microscopy. We show that the initial growth follows the Stranski–Krastanov mode, where islands form on top of a wetting layer consisting of two monolayers (ML) of TiO_2. The epitaxial islands subsequently nucleate and coalesce into large commonly oriented crystallites. The reconstruction observed by reflection high-energy electron diffraction (RHEED) is shown to result from the coexistence of individual (4×1) and (1×4) reconstructions present on different crystallite surfaces. The anatase grows in units of bilayers, resulting in a step height of 2 ML (~0.5 nm). This result explains the fact that the measured period of the RHEED specular-beam intensity oscillations corresponds to the time required for deposition of 2 ML. Ar ion sputtering and UHV annealing results in a transformation to coexisting (4×1) and (1×4) reconstructed terraces on individual crystallites, as commonly observed by ex-situ STM studies.

1. Introduction

Titanium dioxide (TiO_2) is a wide-gap semiconductor of significant interest because of its scientific and technological importance. TiO_2 has attracted much attention because of its potential utility in hydrogen production via water splitting [1], environmental remediation [2], and dye-sensitized solar cell fabrication [3]. TiO_2 exists in nature as three polymorphs — rutile, anatase, and brookite. The TiO_2 anatase polymorph exhibits superior photocatalytic properties [4,5], but is thermodynamically less stable than rutile. Brookite exists in certain mineral formations. Heteroepitaxial growth of anatase is a powerful and unique way to fabricate model surfaces of the less stable anatase polymorph for fundamental surface science studies. Anatase (001) films have been grown epitaxially on perovskite substrates such as $SrTiO_3(001)$ (STO) and $LaAlO_3(001)$ (LAO) by chemical vapor deposition (CVD) [6,7], pulsed laser deposition [8–10], reactive sputtering [11], and molecular beam epitaxy (MBE) [12–16]. In particular, MBE-grown anatase (001) films with various dopants, including Co, Cr, Fe, and N, have been investigated for potential use as ferromagnetic semiconductors and visible-light photocatalysts [17–20].

The unit cell of anatase is tetragonal with lattice constants *a* and *c* equal to 3.78 and 9.52 Å, respectively. The lattice constants of the cubic perovskites STO and LAO are 3.905 and 3.79 Å, respectively. Relatively small lattice mismatches allow anatase (001) to grow epitaxially on (001)-oriented STO and LAO substrates with a cube-on-cube orientation [i.e., $(001)_{anatase}$ || $(001)_{STO}$ and $[100]_{anatase}$|| $[100]_{STO}$]. Coexisting (1×4) and (4×1) reconstructions of anatase (001) have been detected by low-energy electron diffraction (LEED) [21,22], mass spectroscopy of recoiled ions (MSRI) [21], reflection high-energy electron diffraction (RHEED) [13,20,22], and have been directly imaged by scanning tunneling microscopy (STM) and non-contact atomic force microscopy (NC-AFM) [13,20,23,24]. This reconstruction was best explained by the "added molecule (ADM)" structure [25], in which surface tensile stress was relieved by rows of TiO_3 species periodically replacing rows of surface bridging oxygen in the (1×1) surface. This structure was shown to be energetically more favorable than the unreconstructed (1×1) surface and other proposed reconstruction models [25]. It should be noted that all previous STM and AFM studies were done ex-situ. As a result, cycles of Ar ion sputtering and annealing were required to clean the surface after a through-air transfer from the MBE chamber to the STM chamber. The resulting STM and AFM results show that the surfaces are dominated by two types of mutually orthogonal reconstructions separated by single-monolayer (ML) steps of height 2.4 Å (1/4 the height of an anatase unit cell). However, comparison of actual film thicknesses to thickness predictions from RHEED specular-beam intensity oscillations measured during MBE deposition shows that the period of the latter corresponds to the time required to deposit 2 ML, rather than 1 ML [15,26,27]. Thus, it is expected that surfaces with 1/2 unit cell step heights are generated, rather than 1/4 unit cell step heights, as observed in scanning probe images obtained ex-situ. This discrepancy remains unexplained in the literature.

In our previous studies, we have shown that the growth temperature and deposition rate play a critical role in determining film quality

* Corresponding author. Tel.: +1 509 371 6512; fax: +1 509 371 7866.
E-mail address: yingge.du@pnnl.gov (Y. Du).

0039-6028/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.susc.2012.05.010

[26,27]. A higher substrate temperature (650 °C) and a slower growth rate (0.03 Å/s) lead to the highest crystalline quality in phase-pure anatase. However, ex-situ STM studies show that even the best films consist of a mixture of small, orthogonal domains of area<~2000 nm^2 [13,20,24,28]. It is known that local structures such as steps, vacancies, and other atomic-level defects play a crucial role in promoting chemical reactions on metal oxide surfaces [4]. In order to isolate those effects and establish unambiguous structure–property relationships, single-crystal surfaces with fewer defects and larger terraces are highly desirable.

In this report, the growth of TiO_2 anatase films on Nb-doped $SrTiO_3$(001) at elevated temperature by MBE is studied by in-situ STM. We show that the initial growth follows the Stranski–Krastanov mode, where islands form on top of a wetting layer consisting of 2 ML. Further deposition leads to island formation, followed by island coalescence into larger crystallites, or platelets, each with a unique surface reconstruction (either (4×1) or (1×4)), and, ultimately, the formation of well-defined epitaxial TiO_2(001) films with a step height of 2 ML. Sputtering and annealing of epifilms grown ex-situ leads to the formation of smaller mixed (1×4) and (4×1) reconstructions separated by 1 ML step height. In addition, we show that the nucleation and growth of anatase films are influenced by Nb doping in the STO substrates.

2. Experimental details

TiO_2 thin films were grown on Nb-doped (0.02 to 0.7 at.%) STO(001) substrates by MBE in two systems: (i) an ultra-high vacuum (UHV) STM system equipped for oxide film growth [29], and, (ii) a custom-designed three-chamber oxide MBE system. The STM system is equipped with a variable temperature STM (Omicron), an Al X-ray source (Physical Electronics), a hemispherical electron energy analyzer (Omicron), a mass spectrometer (Ametek), an electron gun (VG), an ion gun (SPECS), a high-temperature effusion cell, and an oxygen doser terminated ~1 cm from the substrate. The custom MBE system has been described elsewhere [30,31].

STO(001) substrates were sonicated in acetone and isopropanol and then etched in buffered HF and annealed in flowing O_2 at 950 °C for 8 h. The etching selectively dissolves the SrO layer and the anneal results in an atomically-flat, TiO_2 terminated surface with a minimum step height of 0.4 nm (2 ML or 1 unit cell of STO) [32]. After loading into the STM growth chamber, the substrates were exposed to molecular oxygen at a chamber pressure $\geq6\times10^{-6}$ Torr at 750 °C for 1 h. There was no indication of reduced Ti(III) in the Ti *2p* XPS after annealing, and this treatment removed the surface carbon contamination, but left some residual fluorine, most likely from the HF etch process [20,28,33]. The Ti beam was generated using a high-temperature effusion cell monitored by a quartz crystal microbalance (QCM). The actual film growth rate was calibrated by STM to be ~0.012 Å/s. All films were grown at a substrate temperature of 750 ± 30 °C unless otherwise noted, as judged by a two-color infrared pyrometer (Ircon). The O_2 pressure during growth was $\geq6\times10^{-6}$ Torr, which was sufficient to fully oxidize Ti to Ti(IV). The growth process was interrupted periodically for in-situ STM measurements. STM tips were fabricated from electrochemically etched W wire and were cleaned in-situ by annealing and ion sputtering [34]. Empty-state STM images were collected in a constant-current (0.1-0.3 nA) mode with positive sample bias voltages between 2.0 and 5.0 V. The resulting images were processed using WSxM software [35]. The same growth parameters were used in the MBE system to compare with previous studies and acquire RHEED patterns.

3. Results and Discussion

3.1. Initial stages of TiO_2 growth

An empty-state STM image for a clean Nb-doped STO(001) vicinal surface with 0.5° miscut is shown in Fig. 1 (a). Here we choose the miscut sample to illustrate the effect of step edges on anatase growth, and to use the step height at the edges of terraces as an internal reference for film heights. As we will show in the next section, for STO substrates without miscut, the effect of step edges on anatase growth is not clear in high-resolution STM images as the spacing between steps are normally larger than 200 nm. TiO_2-terminated terraces with an average width of ~50 nm and a minimum step height of 4 Å (1 unit cell of STO) are clearly seen in Fig. 1 (a), as expected based on the preparation method [32]. The starting surfaces in this study are atomically flat and show no sign of surface reconstruction, but it should be noted that in certain conditions, annealing STO in oxidizing environment can lead to different TiO_2-rich reconstructions or re-growth [36–39]. After depositing 0.5 ML, two types of new features, labeled A and B, are identified in Fig. 1 (b). Continuous overlayers (feature A) are observed along the step edges, while islands (feature B) are located on flat terraces. Evidently, feature A represents film growth at step edges and feature B represents nucleation on flat terraces. The line scans presented in panel (b) show that both features are of the same height (~5 Å), and are 1 Å higher than the STO steps. This height matches that of two ML of anatase (4.76 Å), in agreement with previous AFM data for films grown by CVD [7]. Features A and B cover ~28% of the surface, rather than 50%, as expected if the entire 0.5 ML-equivalent deposition formed a film of height equal to 1/4 *c* for anatase. However, such coverage is anticipated for the formation of 2 ML-height features. Atomic resolution was not achieved here, likely indicating that the surface is not well ordered. It should be noted that films grown by PLD showed rather different morphology with an absence of the 2D islands [10], while the

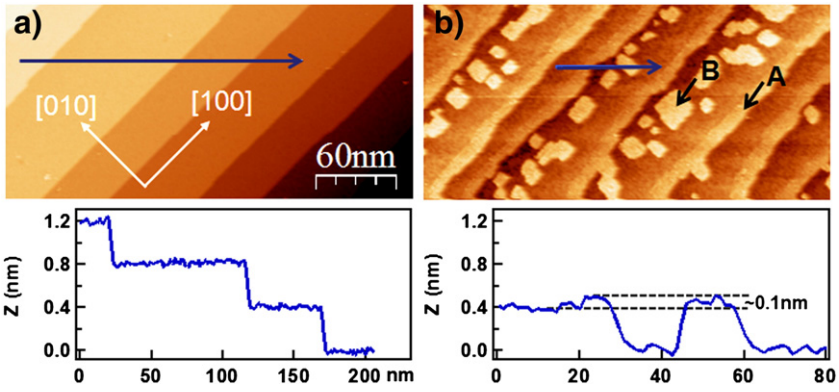

Fig. 1. STM images of a clean STO(001) substrate (a) and the surface after 0.5 ML of TiO_2 deposition (b). The line profiles along the arrows are shown below the images.