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Optimisation of anatase TiO_2 thin film growth on $LaAlO_3$(0 0 1) using pulsed laser deposition

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ABSTRACT

Optimisation of epitaxial anatase TiO_2 thin films grown on $LaAlO_3$(0 0 1) substrates was performed using ultra-high vacuum based pulsed laser deposition (PLD) and studied by in-situ reflection high-energy electron diffraction (RHEED). In addition, ex-situ X-ray diffraction (XRD), atomic force microscopy (AFM), and scanning transmission electron microscopy (STEM) were performed to characterise the bulk properties of these thin films. The deposited TiO_2 thin film is demonstrated to have anatase phase and bonded directly to the $LaAlO_3$(0 0 1) substrate. In a separate ultra-high vacuum system low-energy electron diffraction (LEED) and scanning tunneling microscopy (STM) measurements were performed and a well-ordered two-domain (1×4) and (4×1) reconstruction of anatase surface was observed. Analysis of the STM measurements indicates the coexistence of atomic steps of both 2.5 Å and 5.0 Å, confirming the existence of two TiO_2 domains. The atomic resolution STEM images reveal that the $TiO_2/LaAlO_3$ interface to be terminated with LaO layer and that the anatase-TiO_2 reconstruction was found to be stable during the film growth.

1. Introduction

Titania, TiO_2, has a wide range of applications and a large number of extremely interesting properties. A key 'low-tech' application that stems not only from its optical properties, but also its non-toxicity, is use as a whitening agent in paints and paper. However, applications that more directly stem from its surface properties, as well as the bulk, arise in heterogeneous catalysis including photo-catalysis [1,2], the photovoltaic effect [3,4], and collar cells [5], and it is these applications that are at least part of the reason why TiO_2 is almost certainly the most studied of all oxides surface [6]. Until now, the majority of studies of TiO_2 have been performed on the rutile phase [7–9]. Rutile is the thermodynamically equilibrium phase of TiO_2 at ambient pressures, but two other isomorphs, anatase and brookite also occur naturally. Crucially anatase appears to be the equilibrium phase for small particles with dimension less than 11 nm [2]. It is therefore generally believed that anatase is the active component in many titania based heterogeneous catalysts [4,10] and in current solar cell applications based on nano-crystalline material. As such, there is a clear need to gain a better understanding of the anatase surface structure and the role of the TiO_2 growth conditions (e.g., substrate temperature, oxygen pressure—during growth and annealing, etc.). Thin films of TiO_2 can be formed on a wide variety of substrates including oxide surfaces such as: MgO [11], $SrTiO_3$ [11,12], and $LaAlO_3$ [11–13]. Different deposition methods such as reactive sputter deposition [14], oxygen plasma assisted molecular beam epitaxy (PAMBE) [12,15] or pulsed laser deposition (PLD) [13,16–22] have all been used to fabricate the anatase phase. Until now of the substrates examined, $LaAlO_3$ (LAO) gives the best coherency owing to its relatively small lattice mismatch with anatase. In the bulk phase, anatase TiO_2 has a tetragonal structure with a lattice parameters $a = 0.3776$ nm and $c = 0.9486$ nm, while $LaAlO_3$ can be described as a pseudo-cubic perovskite with a lattice parameter $a = 0.3792$ nm, leading to a mismatch of only 0.4% when TiO_2 is grown epitaxially on the (0 0 1)

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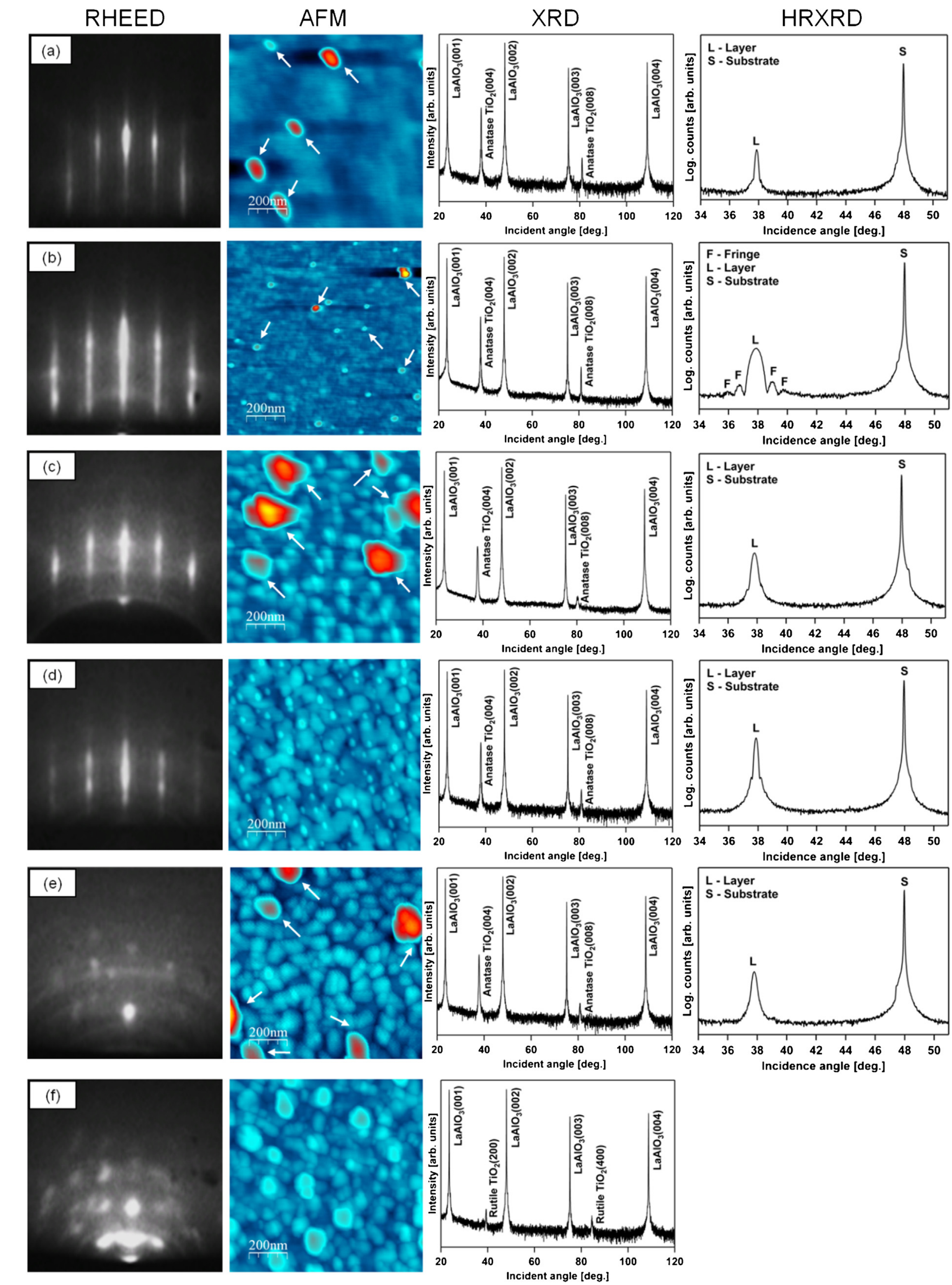

Fig. 1. RHEED, AFM, XRD and HRXRD results of TiO_2 on $LaAlO_3$(0 0 1)—Samples A–F (described in Table 1). The quality of the TiO_2 thin films depends strongly on the growth conditions. (a) Sample A—different laser energy; (b) sample B—different sample-target distance; (c) sample C—oxygen pressure changed during sample annealing; (d) sample D—sample temperature during growth T = 670 °C; (e) sample E—sample temperature during growth T = 690 °C; (f) sample F—different laser pulse frequency.

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