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Combinatorial substrate epitaxy: A high-throughput method for determining phase and orientation relationships and its application to $BiFeO_3/TiO_2$ heterostructures

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Abstract

A new technique, combinatorial substrate epitaxy, has been used to study the polymorphic stability and orientation relationships (ORs) for TiO_2 thin films grown by pulsed laser deposition on polycrystalline $BiFeO_3$ at 600 °C. Electron backscatter diffraction data from 150 substrate/film pairs were analyzed to determine that anatase (A) grew with the OR $(1\,1\,2)_A \| (1\,1\,1)_{BFO}$ and $[1\,\bar{1}\,0]_A \| [1\,\bar{1}\,0]_{BFO}$ on $BiFeO_3$ (BFO) substrates oriented within 35° of [100]. Rutile (R) was found on all other substrate orientations with $(1\,0\,0)_R \| (1\,1\,1)_{BFO}$. The in-plane orientation was primarily $[0\,0\,1]_R \| [1\,\bar{1}\,0]_{BFO}$, but some films near the anatase/rutile phase boundary were rotated by 30° so that $[0\,0\,1]_R \| [\bar{1}\,2\,\bar{1}]_{BFO}$. Because these substrate film pairs have high-index interface planes, conventional epitaxy arguments based on two-dimensional lattice mismatch in low-index planes are considered to be limiting cases of a more general model involving the three-dimensional alignment of closest packed planes and directions, regardless of the interface plane.

Keywords: Epitaxy; Crystal growth; EBSD; Interfaces; Orientation relationships

1. Introduction

TiO_2 films on $BaTiO_3$ substrates have been shown to exhibit novel photochemical activity, including spatially localized reactivity governed by the underlying ferroelectric domain structure [1–3]. More recently, it has been demonstrated that when TiO_2 is supported on ferroelectric $BiFeO_3$, it demonstrates a similar spatially selective reactivity, but is also photochemically active in visible light (unlike bulk TiO_2 or TiO_2 supported on $BaTiO_3$) [4]. Titania films crystallize in both the rutile and anatase structures when deposited on perovskite-structured $BiFeO_3$. Because the photochemical reactivity of titania is known to depend on both its phase [5] and orientation [6–8], it is of interest to determine the orientation relationships (ORs) for $BiFeO_3/TiO_2$ heterostructures.

Currently, little is known about the crystallization preferences of films on high-index surfaces. Epitaxy in thin films is usually ascribed to preferred lattice matching at low-index two-dimensional interfaces [9]; the extension of such theories to high-index surfaces is difficult. To better understand the nature of crystallization of films on general surfaces, it is necessary to observe growth over the entire range of possible surface orientations. The conventional approach of growing films on large-area, low-index, single-crystal substrates is not practical for a comprehensive study of growth on high-index surfaces.

This paper has two purposes. The first is to describe a new high-throughput technique we refer to as "combinatorial substrate epitaxy" (CSE) to determine phase relationships and ORs between a substrate and deposited film for all possible orientations. In the CSE approach, films are

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deposited on hundreds of substrates with different, known orientations in a single experiment and then characterized by electron backscatter diffraction (EBSD). The second purpose is to describe the specific phase and ORs in the $BiFeO_3/TiO_2$ system and show that epitaxy in this system is driven by the alignment of close-packed planes and directions in three dimensions.

Although $BiFeO_3$ is trigonal, the distortion from cubic is small ($\alpha = 89.3°$) and it can be considered as a pseudocubic perovskite ($a = 3.96$ Å); this simplification will be made throughout this paper [10]. While the ORs in $BiFeO_3/TiO_2$ heterostructures have not been reported before, there have been a number of studies reporting the growth of TiO_2 on $LaAlO_3$ ($a = 3.790$ Å [11]), $SrTiO_3$ (3.905 Å [12]) and $BaTiO_3$ (3.9920 Å [12]) [13–27]. While the experiments span a range of materials, temperatures and growth techniques, there are a few common features. The first is that for growth on (0 0 1) oriented substrates, the most common OR is $(0\,0\,1)_A \| (0\,0\,1)_P$ and $[1\,0\,0]_A \| [1\,0\,0]_P$, where A denotes anatase and P denotes perovskite [13–16,19,20,23,25–27]. The second common feature is that on perovskite (1 1 1), rutile grows in the (1 0 0) orientation [13,21,22,27]. These observations have been rationalized using lattice-matching arguments; the relevant lattice parameters are listed in Table 1 [10–12,28,29].

With the exception of the paper by Burbure et al. [13], all of the previous studies used single-crystal substrates with low-index orientations. Burbure et al. [13] grew TiO_2 films on a polycrystalline $BaTiO_3$ substrate and used EBSD in a scanning electron microscope to determine the orientations of the substrate and film grains. In the present paper, we present a technique based on the same experimental concept, but with an improved analysis method that makes it easier to determine the ORs. Through the analysis of 150 $BiFeO_3$ substrate/TiO_2 film pairs, the range of substrate orientations that stabilize epitaxial anatase and rutile have been determined as well as the ORs for each of these phases. In the vast majority of the cases, epitaxial growth occurs on high-index planes and aligns the close-packed planes and directions that are common to each phase.

2. Experimental methods

A polycrystalline $BiFeO_3$ substrate was synthesized from Bi_2O_3 (Alfa Aesar 99.99%) and Fe_2O_3 (99.945%) powders [30]. Equimolar amounts of both powders were mixed and ball milled in ethanol for 24 h, and dried at 85 °C. The mixture was calcined in air at 700 °C for 3 h to form $BiFeO_3$ powder, as verified by X-ray diffraction.

Table 1
Crystallographic parameters for $BiFeO_3$ and TiO_2 [10–12].

Phase	Space group	Lattice parameter
$BiFeO_3$	$R3c$	$a = 3.962$ Å, $\alpha = 89°31'$
Anatase TiO_2	$I4_1/amd$	$a = 3.785$ Å, $c = 9.514$ Å
Rutile TiO_2	$P4_2/mnm$	$a = 4.594$ Å, $c = 2.958$ Å

The $BiFeO_3$ powder was ground, ball milled in ethanol for 24 h, dried and compressed uniaxially at 105 MPa to form a pellet ~1 cm in diameter and 3 mm thick. The $BiFeO_3$ pellet was sintered at 850 °C for 3 h. One side of the pellet was ground with an aqueous Al_2O_3 suspension (3 μm, Logitech) and polished with a SiO_2 colloidal suspension (0.02 μm, MasterMet 2, Buehler) using a Logitech autopolisher. The polished pellets were then annealed at 600 °C for 3 h in air to heal polishing damage.

After preparing the $BiFeO_3$ substrate, the orientation of each grain within an area of approximately 1.2×1.2 mm^2 on the surface was determined using EBSD in a Quanta 200 scanning electron microscope (FEI, Hillsboro, OR) [31]. The substrate surface was tilted at 70° with respect to the beam direction in high vacuum (10^{-5} torr). The beam energy was set at 25 keV, the spot size was 5.5 and the working distance was 15 mm. The Kikuchi patterns were indexed using TSL orientation imaging microscopy data collection and analysis software (EDAX, Mahwah, NJ). The orientation data was processed as described previously [30].

After the substrate orientations had been measured, a TiO_2 film was grown on the $BiFeO_3$ substrate using pulsed laser deposition (PLD) [32]. The TiO_2 target was synthesized by compressing TiO_2 powder in a die to form a disc ~2.5 cm in diameter and ~1.4 mm thick, and then sintering it at 1400 °C for 12 h. Before depositing the TiO_2 film, the chamber was pumped down to reach a base pressure of 10^{-5} torr with the substrate heated to 120 °C. Oxygen was then introduced to the chamber and a partial pressure of 5 mTorr was maintained. The substrate was then heated to 600 °C at a rate of 25 °C min^{-1}. A KrF ($\lambda = 248$ nm) laser with an energy density of 2 J cm^{-2} was pulsed at 3 Hz for 10 min to clean the target. During the deposition, the target-to-substrate distance was maintained at approximately 6 cm. The deposited film was estimated to be 100 nm thick, based on the number of laser pulses and the measured deposition rate, as reported previously [4]. After the deposition, the substrate was cooled to room temperature at a rate of 25 °C min^{-1} in an atmosphere of 5 torr stagnant oxygen.

The TiO_2 film on the $BiFeO_3$ substrate was characterized by EBSD using a procedure that is similar to that used for the $BiFeO_3$ substrate. One source of error in the determination of the OR stems from alignment of the sample during the orientation mapping. Because the sample is removed from the microscope after the substrate mapping, and then returned for mapping the film, a small misalignment will result in a constant average misorientation between the substrate and film data that will be superimposed on the typical uncertainty associated with the orientation measurement.

The procedure for finding the ORs begins by manually matching substrate grains with film grains by visual inspection of orientation maps, such as those shown in Fig. 1. For example, based on the similar position and shape, one can deduce that the grains marked by the same symbols (A–D) on the substrate (Fig. 1a) and in the film (Fig. 1b) correspond to pairs. This makes it possible to create a list of matched pairs, in which the unique "grain