Available online at www.sciencedirect.com
ScienceDirect
Surface Science 600 (2006) L219–L223
SURFACE SCIENCE
www.elsevier.com/locate/susc

Surface Science Letters

$SrTiO_3(001)$ reconstructions: the (2×2) to $c(4 \times 4)$ transition

Fabien Silly, David T. Newell, Martin R. Castell *

Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, UK

Received 27 March 2006; accepted for publication 23 May 2006
Available online 16 June 2006

Abstract

Scanning tunneling microscopy (STM) is used to investigate the (001) surface structure of Nb doped $SrTiO_3$ single crystals annealed in ultra high vacuum (UHV). Atomically resolved images of the (2×2) reconstructed surface are obtained after annealing a chemically etched sample. With further annealing dotted row domains appear, which coexist with the (2×2) reconstruction. The expansion of these domains with further annealing gives rise to the formation of a TiO_2 enriched $c(4 \times 4)$ reconstruction.

Keywords: Scanning tunneling microscopy; Surface relaxation and reconstruction; Alkaline earth metals; Titanium; Surface structure, morphology, roughness, and topography; Low index single crystal surfaces; Surface defects

Strontium titanate has attracted much attention as a model perovskite system. Its bulk, thin film, and small particle structure [1–5], as well as its electronic properties [6–13] have been extensively investigated. $SrTiO_3$ has been used as a lattice matched substrate for the growth of high temperature superconductors [14,15]. It was also successfully used as a support for metal thin film and nanocrystal growth for Au [16,17], Pd [18–21], Pt [22] Co [23], Cu [24], Ni [25], Fe [26], Mo [27], Ir [28], Cr [29], Ag [30] as well as a support for the formation of TiO_x islands [31–33], Sr [34] and SrO rich islands [35], and perovskite nanodots [36]. Heteroepitaxial growth on $SrTiO_3$ has highlighted the importance of the nature of the surface. $SrTiO_3(001)$ has the ability to support numerous surface reconstructions. Changes in surface reconstruction can be the key parameter that determines nanocrystal shape, as in the case of Pd [18]. To date the reconstructions reported include (1×1), (2×1), (2×2), $c(4 \times 2)$, $c(4 \times 4)$, $(\sqrt{5} \times \sqrt{5})R26.6°$, $(\sqrt{13} \times \sqrt{13})R37.7°$, (6×2), $c(6 \times 2)$ and (9×2) [21,23,1,37–46,34,47–50]. Technological applications of this material require the optimization of the processes that can reproducibly produce a given surface structure. In this paper, we report on STM studies of the reconstructions of an HF etched $SrTiO_3(001)$ substrate under annealing conditions in UHV. We show that a (2×2) reconstruction forms at low temperature. Further annealing gives rise to the appearance of domains of linear structures that coexist with the (2×2) reconstruction. We then show that the expansion of these domains with annealing time results in the formation of a $c(4 \times 4)$ reconstruction.

$SrTiO_3$ is a cubic perovskite with a 3.905 Å lattice parameter. In its pure form it has a 3.2 eV band gap which makes it unsuitable for imaging with the scanning tunnelling microscope (STM). To overcome this problem we use crystals doped with 0.5% (weight) Nb. These crystals were supplied by PI-KEM, UK, with epi-polished (001) surfaces. $SrTiO_3(001)$ samples were prepared by chemically etching the crystals in a buffered NH_4F–HF solution and introduced into the ultrahigh vacuum (UHV) chamber of a STM (JEOL JSTM4500S) operating at a pressure of 10^{-10} mbar. Etched tungsten tips were used to obtain constant current images at room temperature with a bias voltage applied to the sample. Resistive sample heating in the UHV chamber was achieved by passing a current through the sample. Temperature measurement was performed through a viewport using a disappearing filament optical pyrometer.

* Corresponding author.
E-mail address: martin.castell@materials.ox.ac.uk (M.R. Castell).

0039-6028/$ - see front matter
doi:10.1016/j.susc.2006.05.043

Fig. 1 shows the surface of an etched $SrTiO_3(001)$ sample annealed in UHV at 950 °C for 2 h. A high resolution STM image (Fig. 1a) shows a surface with a square lattice reconstruction orientated along the crystallographic axes of the sample. The measured ⟨100⟩ periodicity along this lattice is 8.0 Å. This corresponds to a (2×2) reconstruction and covers the entire surface of the sample. The irregular dark and bright features on the surface are most likely due to crystal defects such as O vacancies or Nb dopants. The image labeled Fig. 1b shows two step edges on this surface separating three flat terraces. The step edges are wavy and show no preferential crystallographic orientation. The wavy step edges are similar to those of the (2×1) reconstruction, but are unlike the oriented steps reported on the $c(4 \times 2)$ reconstruction [37]. The step heights are 3.95 ± 0.14 Å (Fig. 1c), corresponding to one $SrTiO_3$ unit cell height.

Fig. 2 shows STM images of the $SrTiO_3(001)$ sample after the (2×2) surface was annealed at 1030 °C for 1 h. Fig. 2a shows that domains (bright areas) are now visible on the (2×2) terraces (dark area). An image at higher magnification (Fig. 2b) shows that these domains are composed of lines of bright spots oriented along the ⟨110⟩ directions. The majority of the visible lines exist as single or double rows of bright spots. The measured periodicity along each row is 11.06 Å which corresponds to the length of the diagonal of the (2×2) surface unit cell. A high resolution image of the junction between the two different domains is presented in Fig. 2c. In this image we see a domain consisting of the dotted row domain on the left, whilst on the right the (2×2) surface reconstruction is atomically resolved. It should be noted that the dotted rows shown in Fig. 2 are

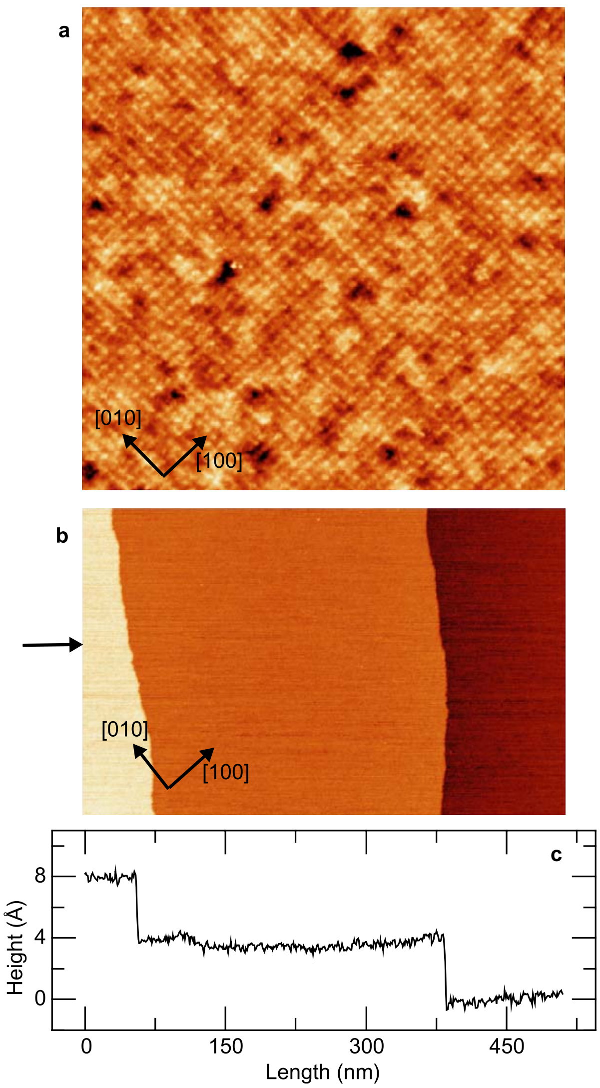

Fig. 1. STM data from the $SrTiO_3(001)$-(2×2) reconstructed surface. The atomic periodicity is shown in the 35×35 nm^2 image in (a); $V_s = +0.7$ V, $I_t = 0.3$ nA. In (b) two wavy step edges separating three terraces are shown; 510×325 nm^2, $V_s = +0.8$ V, $I_t = 0.3$ nA. The black arrow in (b) indicates the position of the height profile shown in (c), which shows that the terrace steps are around 4 Å or one unit cell high.

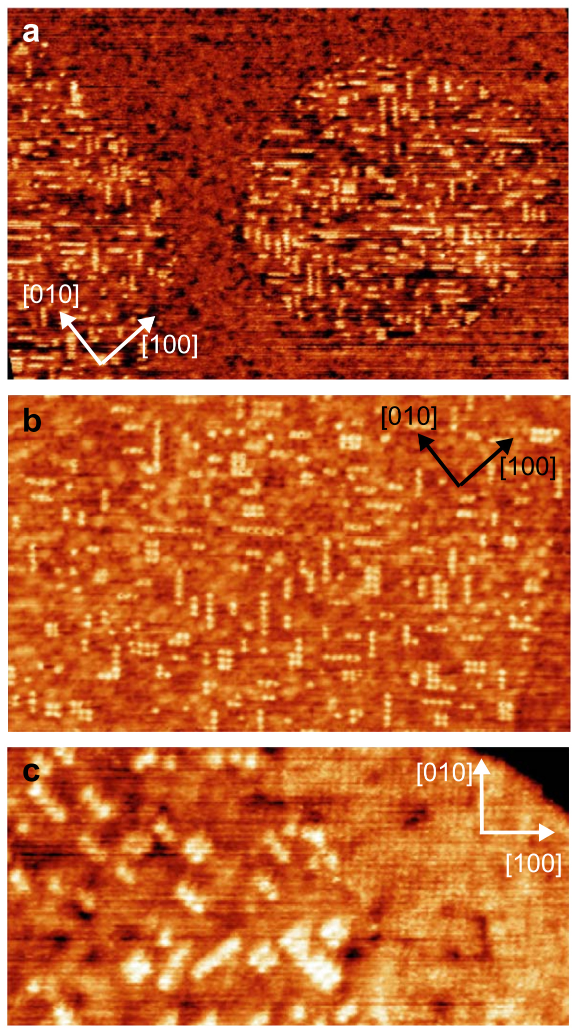

Fig. 2. STM images of dotted row structures on the $SrTiO_3(001)$-(2×2) surface. In (a) the brighter regions are the dotted row domains; 150×100 nm^2; $V_s = +1.0$ V, $I_t = 0.3$ nA. The image in (b) shows a dotted row domain in more detail; 85×50 nm^2; $V_s = +1.0$ V, $I_t = 0.3$ nA. In (c) a dotted row domain and the (2×2) surface are shown; 54×27 nm^2; $V_s = +0.8$ V, $I_t = 0.3$ nA.