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Surface engineering along the close-packed direction of SrTiO₃

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Abstract

We have investigated the effects of wet etching with a 3:1 mixture of HCl:HNO₃ and of annealing at 850°C on the surface morphology of [1 1 1]-oriented SrTiO₃ single crystals. Atomic force microscopy is used to demonstrate that the surface morphology is a strong function of both etching and annealing time. All surfaces have step heights equal to integral or half-integral multiples of the (1 1 1) interplanar spacing. However, step bunching, non-regular step heights, granularity, inhomogeneous surface morphology, and etch pits are observed on many surfaces. A combination of etching and annealing leads to surfaces that are free of these irregularities and are characterized by well-developed step-terrace structures: the terraces are ≈ 600 Å wide, the step heights are either 1.2 Å or 2.3 Å, which are a half or a whole (1 1 1) interplanar distance, respectively, and the step edges are parallel to a single $\langle 1 1 0 \rangle$ -type direction. The existence of these two step heights implies that the surfaces are terminated by both SrO₃ and Ti planes. © 2001 Elsevier Science B.V. All rights reserved.

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Many processes, including catalysis and thin film growth, depend critically on the structure and chemistry of surfaces. In spite of this, structural and physicochemical properties of many important surfaces remain poorly understood. For complex oxides, this is in part a result of the difficulty in reproducibly obtaining well-defined surfaces. Considerable attention has been paid recently to engineering oxide surfaces because of their preeminent role in the growth of high quality epitaxial thin films [1–7].

[1 0 0]-oriented SrTiO₃ is widely used as a substrate for thin film growth. High temperature annealing in oxygen [2] or UHV and solution

chemical treatments [1,4] have been developed to produce atomically smooth and chemically pure surfaces that have a regular step-terrace structure characterized by a single step height (equal to the unit-cell parameter), a uniform terrace width (determined by the miscut), and a single type of terminating plane (TiO₂). The surface chemistry can be further controlled in a second step and the surface can be converted from TiO₂ to SrO layers by depositing a monolayer-thick film of SrO [6,8] or Sr₂TiO₄ [9].

Such well-defined surfaces, which are ideal for thin film growth, have not been obtained for the polar surfaces of [1 1 1]-oriented crystals. Surfaces of [1 1 1]-oriented SrTiO₃ have been studied using RHEED, LEED, STM [10,11], and ex situ AFM after high temperature annealings in oxygen or argon atmospheres [12]. On these surfaces, both

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possible surface terminations, SrO_3^{4-} and Ti^{4+} , and various morphologies have been reported, but not well-developed step and terrace structures.

Well-defined surfaces on [1 1 1]-oriented SrTiO_3 , i.e., along the close-packed direction of this prototypical perovskite, are important for fundamental studies on the mechanisms of thin film growth and developing new materials. Recently, superlattices deposited upon [1 1 1]-oriented SrTiO_3 were grown in the LaFeO_3 – LaCrO_3 systems; their unique structural order was used to confirm theoretically predicted Fe^{3+} – O^{2-} – Cr^{3+} magnetic interactions [13]. Developing other novel superlattices and artificial structures is of interest from many scientific and technological points of view, and this requires a better understanding of the chemical and morphological stability of specific polar surfaces. In this paper, we report on the effects that wet chemical etching and annealing have on the surface morphology of [1 1 1]-oriented SrTiO_3 .

Mechano-chemically polished, [1 1 1]-oriented (0.5 mm thick, miscut $<0.5^\circ$, rms roughness $\approx 2 \text{ \AA}$) SrTiO_3 single crystals were obtained from Crystal GmbH (Berlin). These single crystals were cut with a diamond wire saw to reduce the dimensions to $3 \text{ mm} \times 5 \text{ mm}$. Such samples were cleaned ultrasonically in acetone then in alcohol, and they are termed as-delivered samples. Some samples were subjected to chemical treatments similar to those developed for [1 0 0]-oriented SrTiO_3 [4,7,14]. Samples were first soaked in water for 30 min and were then etched in a 3 : 1 solution of $\text{HCl} : \text{HNO}_3$ for a time varying between 0.5 and 8 min. The samples were immediately rinsed in water and dried by a heat gun. Annealings were carried out on both as-delivered and etched samples. Samples were attached to the heater in our PLD chamber with silver paint and annealed at a temperature of 850°C for a time between 1 and 60 min. The heating rate was $15^\circ\text{C}/\text{min}$, the annealing was performed in a dynamic vacuum maintained at 200 mTorr oxygen pressure, and the cooling rate was $20^\circ\text{C}/\text{min}$.

Ex situ AFM measurements were carried out in air using an AutoProbe CP (Park Scientific Instruments) in contact mode with ultralevers tips. To minimize surface contamination resulting from

long exposure to air, AFM experiments were performed immediately after any sample treatments. Step-edge orientation was determined by X-ray diffraction in the back reflection Laue configuration using a Rigaku diffractometer equipped with Mo K_α radiation.

No features of interest were observable on the surfaces of either as-delivered or etched samples without annealing. The rms roughness of the as-delivered samples were $\approx 2 \text{ \AA}$. The rms roughness of a sample etched for 4 min was $\approx 1.3 \text{ \AA}$, a slight improvement over the as-delivered samples. Samples annealed for 30 min without etching had inhomogeneous surfaces with two distinct morphologies. The first morphology had a granular appearance with very small features and was similar to that observed by Tanaka and Kawai [10] on a sample annealed at high temperature in UHV. The other morphology had larger features that were more extended spatially and could be described as irregular terraces with some step bunching. None of the surfaces that were observed on these etched or annealed samples could be considered morphologically well defined. We therefore investigated the effects of combined etching and annealing on the surface morphology.

Fig. 1 shows the surface morphology of samples annealed for 30 min and etched for various times: 0.5, 2, 4, and 6 min correspond to Fig. 1(a), (b), (c) and (d), respectively. The combined etch/anneal leads to a considerable increase in the homogeneity of the surface morphology and an increase in the quality of the step-terrace structures. For all samples, step-terrace structures are evident. In Fig. 1(a), we observe a slightly irregular step-terrace structure with wavy step edges, some step bunching and large white features located on the terrace edges, which are reminiscent of islands. The step heights vary from 1/2 to 2 times the (1 1 1) interplanar distance, $d_{111} = 2.3 \text{ \AA}$, with the larger values corresponding to transitions from the islands.

Longer etching times are very effective at removing these irregularities, as observed in Figs. 1(b)–(d). In Fig. 1(b), a more regular step-terrace structure with a reduced number of islands is observed. The step heights are similar to those found for the sample annealed for 30 s. Further

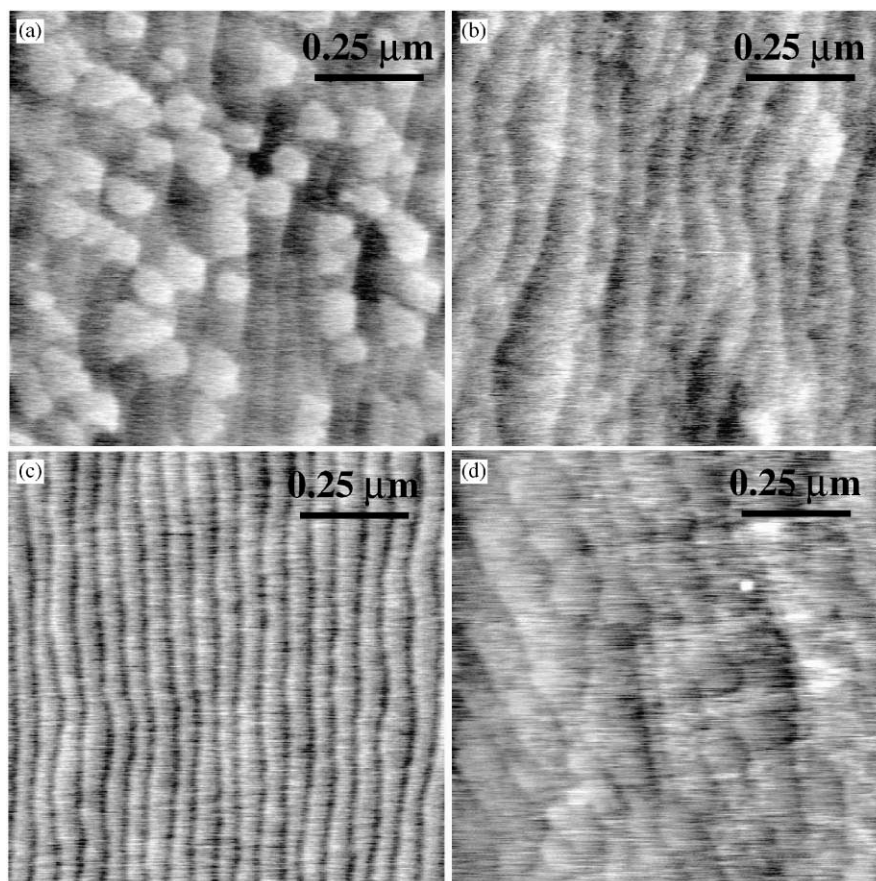


Fig. 1. AFM images of samples etched for varying times and annealed for 30 min at 850°C: (a) 0.5 min (b) 2 min, (c) 4 min, (d) 6 min.

improvement of the morphology is found for the sample etched for 4 min. The surface shown in Fig. 1(c) has a very regular step and terrace structure with straight step edges that remain well defined over the entire surface of the substrate and steps of either $1/2$ or 1 times d_{111} . This surface will be discussed in more detail below. Longer etch times (≥ 6 min) do not lead to a continuing improvement of the surface. Fig. 1(d) shows a surface etched for 6 min that has wavy step edges, less regular terrace widths, and a minor increase in the step heights ($1/2$ – $3/2$ d_{111}). More importantly, large etch pits were observed on samples etched for ≥ 6 min; hence a 4 min etch seems to be optimal.

Fig. 2 illustrates the pronounced effect of annealing time on the surface morphology of samples etched for the optimal time (4 min).

Annealing times for the samples given in Fig. 2 are (a) 1 min, (b) 15 min, (c) 30 min, and (d,e) 1 h. A 1 min anneal leads to a surface that has a poorly formed step-terrace structure. Terraces have wavy edges, irregular sizes, and islands on them. A 15 min anneal leads to terraces that are more evident but that still have wavy edges and islands dispersed upon them. In both cases, the terrace step heights are either $1/2$, 1 , or $3/2$ times d_{111} .

As discussed above, surfaces annealed for 30 min have extremely well-defined step-terrace structures. Such surfaces were highly reproducible and were observed on multiple samples produced in the same manner. The step edges are now straight and run along a single $\langle 110 \rangle$ direction of the crystal, as determined by X-ray diffraction. This is unsurprising since the $[110]$ is the direction

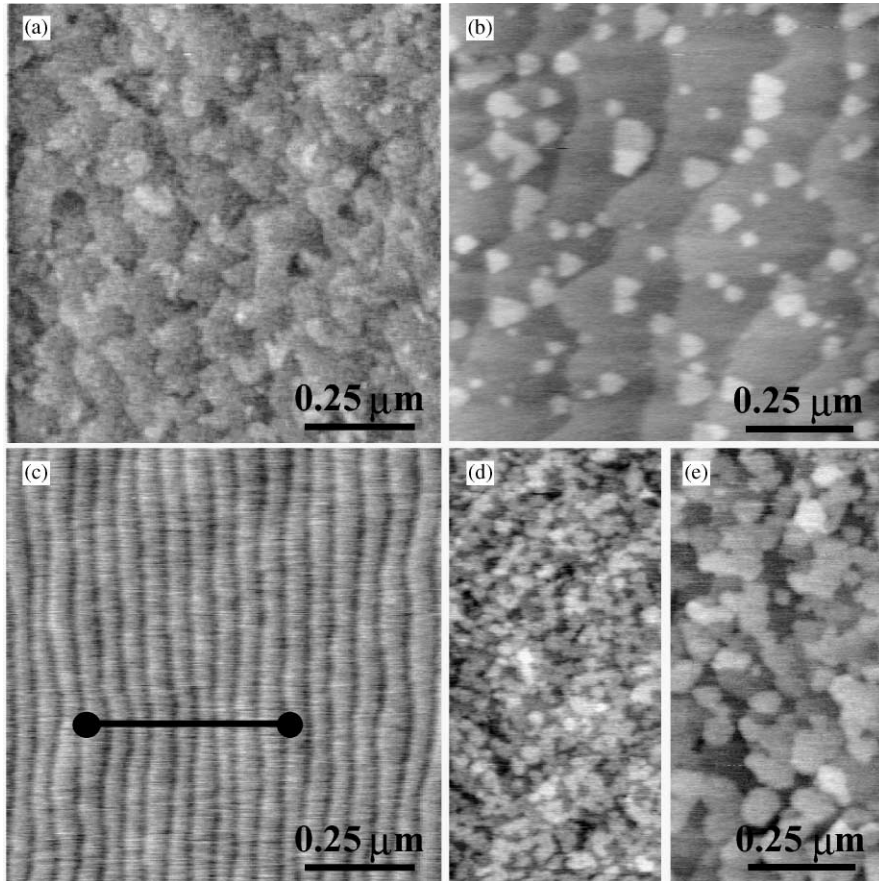


Fig. 2. AFM images of samples etched for 4 min and annealed for various times at 850°C: (a) 1 min, (b) 15 min, (c) 30 min, (d) 60 min. The arrow shows the line for which the profile is shown in Fig. 3.

of closest contact of atoms within the (1 1 1). The terrace widths are uniform and $\approx 600 \text{ \AA}$ wide. The step profile of a region of this sample is given in Fig. 3 and shows the terrace structure consisting of two distinct step heights. The 1.2 \AA transition is equal to $1/2 d_{111}$ and corresponds to a transition between chemically dissimilar planes— SrO_3^{4-} and Ti^{4+} (A to B in the figure). The existence of these half-integral d_{111} steps implies that the surfaces are not chemically pure, even though the step-terrace structure is well-developed. The 2.3 \AA steps are equal to d_{111} and correspond to the transition between chemically similar planes—either $\text{SrO}_3^{4-}/\text{SrO}_3^{4-}$ or $\text{Ti}^{4+}/\text{Ti}^{4+}$ (A to A in the figure). Further work is necessary to attain a chemically pure surface.

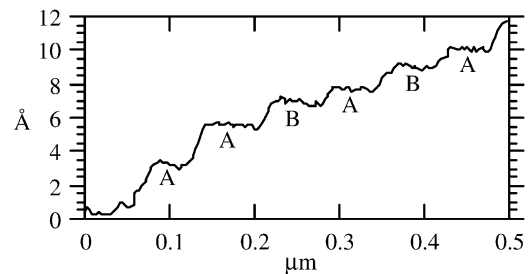


Fig. 3. Topographic profile of sample etched for 4 min and annealed at 850°C for 30 min. The trace is marked in Fig. 2(c).

It is interesting to note that the step height and terrace widths decrease from the 15 to 30 min sample, and also that the step edges straighten

dramatically. Longer anneals, however, do not lead to an increase in the morphological or chemical order of the surface. The morphology of a sample annealed for 1 h is characterized predominantly by very fine plate-like features, as seen in Fig. 2(d), although some regions with larger plate-like features can be observed, illustrated in Fig. 2(e). The step heights in these regions are between 1/2 and 3 times d_{111} , which means a significant roughening has occurred for samples annealed longer than the optimum time. The breakup of the steps observed in Fig. 2(e) implies that the surface is only an intermediate state. An as-delivered sample was annealed at 1200°C in a tube furnace in oxygen for 6 h and large terraces with zig-zag edges (directed along multiple $\langle 110 \rangle$ directions) were observed. Extreme step-bunching resulted in $[110]$ -faceted steps with step heights of several nanometers. This supports the idea of the instability of the (111) surface for our crystals. Nevertheless, it is important to note that the local surface normal of samples annealed at 850°C was always observed to be identical to the global surface normal, i.e., the normals were $[111]$.

We have studied the influence of HCl:HNO₃ wet etching and high temperature annealing on the SrTiO₃ surface along the close-packed direction. Both the etching time and the annealing time strongly influence the final surface morphology. A regular step-terrace structure has been obtained on $[111]$ -oriented SrTiO₃ by combining a wet etch for 4 min with an anneal of 30 min. The observed step heights indicate that two chemically different planes terminate this surface. This implies that, while a morphologically well-defined sample may be obtained under specific conditions, further treatments are required to attain the chemical purity that allows for very basic studies of surfaces or for precisely controlled thin film growth. We are currently investigating methods of removing one of these terminations in a further processing step to produce chemically and morphologically pure

surfaces along the close-packed direction of perovskites.

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