Tuning the termination of the SrTiO$_3$(110) surface by Ar$^+$ sputtering

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We report a scanning tunneling microscopy study on the SrTiO$_3$(110) surface treated with Ar$^+$ sputtering followed by annealing. Two types of termination coexist on the surface, which are spatially identified as the 4 × 1 reconstructed SrTiO layer and the O layer covered by Ti-rich oxide clusters, respectively. The relative areal ratio of the two types is tuned by sputtering dose reproducibly, and monophased surface with either SrTiO or O termination is obtained. The surface is stable at temperatures up to 1100 °C and under oxygen partial pressures from 6 × 10$^{-5}$ mbar to ultra high vacuum, providing us a flexible epitaxial growth template. © 2009 American Institute of Physics. [DOI: 10.1063/1.3180701]

The artificial metal oxide structures display diverse physical properties due to the strong correlations between multiple degree of freedom, reduced dimensionality, broken symmetry, and spatial confinement effects. Much effort has been devoted to the syntheses of low-dimensional oxide systems, especially thin films and superlattices. It is revealed that the terminating layer of the substrate surface plays a crucial role in determining the epitaxial growth and the electronic structure at the interface. Therefore the precise control of the substrate surface at an atomic scale enables the tailoring of oxide heterostructures. Single-crystalline SrTiO$_3$ is widely used as the epitaxial growth substrate for a variety of oxide films. By selective chemical etching of SrO layer, the atomically well-defined (001) surface can be achieved with TiO$_2$ termination. Recently, atomically flat SrTiO$_3$(110) and (111) surfaces are obtained by annealing and chemical etching, respectively.

SrTiO$_3$ single crystal is composed of alternately stacked (SrTiO)$^{4+}$ and (O$_2$)$^{2-}$ atomic layers along [110] orientation, which creates a macroscopic dipole perpendicular to the (110) surface. To study the stability of such a polar surface, various mechanisms of polarity compensation have been proposed: (1) modification of surface charges by partially filling electron surface states; (2) modification of the surface composition; and (3) adsorption of charged species. A wide variety of surface reconstructions were reported on SrTiO$_3$(110) surface and ascribed to (100) and (010) microfaceting. Recently, Russell and Castell obtained the surface without microfaceting that reconstructed along [001] direction only.

It has been reported that the SrTiO$_3$(110) surface polarity has strong influence on the interface ferromagnetism and spin polarization for epitaxial manganite thin films. To study the substrate termination and to understand its stabilization mechanism are important issues. Moreover, a monophased template is a necessity for the precise control of the subsequent epitaxial growth. In this letter, we obtain both SrTiO (type A) and O (type B) terminations on SrTiO$_3$(110) surface by Ar$^+$ sputtering followed by annealing. We spatially identify them by using scanning tunneling microscopy (STM) and reflected high-energy electron diffraction (RHEED). The areal ratio of the two terminations is tuned continuously by adjusting the sputtering dose, covering the range from monophased A- to B-type termination. The surfaces are stable at temperatures up to 1100 °C and under oxygen partial pressures from 6 × 10$^{-5}$ mbar to ultra high vacuum.

The experiments were performed in an Omicron low temperature STM system with the base pressure of 1 × 10$^{-10}$ mbar. Nd-doped (0.7 wt %) SrTiO$_3$(110) single crystals (12 × 3 mm$^2$) were purchased from Heifei KMT Co., China. The as-received sample was sputtered with Ar$^+$ beam at room temperature followed by annealing in ultra-high vacuum (UHV) or under different oxygen partial pressure. The sample was resistively heated by passing a direct current and the temperature was monitored with an infrared temperature sensor.

![ STM image and RHEED patterns](image)

FIG. 1. (Color online) (a) The ball model of the SrTiO$_3$(110) with (Sr/TiO)$^{4+}$ and (O$_2$)$^{2-}$ terminations. Sr, Ti, and O atoms are drawn in gray (green), white, and black (red), respectively. The step height is 1.38 Å. The lower panel shows the top view correspondingly. The surface unit cells are labeled, respectively. (b) An STM image (unoccupied-state, 2.5 V/20 pA) of the cleaned surface, exposing two types of termination labeled with A and B, respectively. (c) Line profile of the surface along the black line in (b), indicating a step height of ~1.38 Å.

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pyrometer. The surface was characterized with RHEED and STM.

Figure 1(b) shows a STM image of the SrTiO$_3$(110) single crystal surface after Ar$^+$ sputtering (500 eV/3.2 μA for 10 min) followed by UHV annealing (1000 °C for 1 h). Two distinct types of domain coexist on the surface, labeled with A and B. A-type domain is characterized by the periodic stripes along [110], B-type is also long-range ordered, covered by dense clusters with random size and spatial distribution. The step height between the two domains is about 1.38 Å, equivalent to the spacing of adjacent (SrTiO)$_4^+$ and (O$_2^-$) planes along [110] orientation. It is indicated that both SrTiO and O terminations are stabilized on the surface.

The monophased SrTiO$_3$(110) surfaces with either A- or B-type termination are obtained by optimizing the preparation parameters (see the following for detail). Figure 2(a) shows a uniform A-type termination achieved by 500 eV sputtering 2.0 μA for 10 min followed by UHV annealing at 1000 °C for 1 h. Each stripe along [110] direction contains three rows of periodic dots with different brightness, separated with a dark trench. Long-range order is formed with the lattice constant of 0.63 ± 0.05 nm along [110] and 1.65 ± 0.1 nm along [001] direction, respectively. Also considering the RHEED patterns along these two directions as shown in Figs. 2(b) and 2(c), we identify the A-type termination as (4 × 1) reconstructed SrTiO$_3$ layer, which has been reported recently.\(^{22}\)

The monophased SrTiO$_3$(110) surface with uniform B-type termination is obtained by sputtering with 500 eV ion beam at 2.8 μA for 13 min followed by UHV annealing at 1000 °C for 1 h. As shown in Fig. 3(a), a rectangular lattice is formed with the unit vector of 0.4 nm along [001] and 0.3 nm along [110] directions, respectively. Note the periodicity along [110] direction is equivalent to that in the unreconstructed (O$_2^-$)$_4^-$ plane, but by half of that in the unreconstructed SrTiO$_3$ plane. This is an unambiguous indication that the B-type termination is the O layer without reconstruction along [110] direction. Such an O-terminated surface is stabilized with the assistance of the densely adsorbed clusters. At high imaging bias, we observe the long-range ordered clusters on the surface [Fig. 3(b)], forming a (6 × 8) superstructure. The fractional patterns in RHEED also represent the consistent periodicity of the top layer, as shown in Figs. 3(c) and 3(d). We conclude that the B-type termination is the O layer while A-type is the SrTiO$_3$ layer, being 1.38 Å apart from each other along [110] direction.

By adjusting the sputtering parameters we are able to tune the termination of SrTiO$_3$(110) surface. The areal ratio of A-type termination through the entire surface, i.e., the $S_A$ value is quantified by the statistics over a number of STM images. $S_A$ is saturated at a certain value after a few cycles (less than 4) of cleaning with fixed sputtering and annealing parameters. No matter how much $S_A$ is on the initial surface, such a “saturated” value is determined by the sputtering dose in each cycle only, but not the total dose accumulated from all the preceding cycles, as shown in Fig. 4(a). We keep all other cleaning parameters constant and investigate the dependence of the saturated $S_A$ on the sputtering dose in each cycle.

![Figure 2](image2.png)  
**FIG. 2.** (Color online) (a) An STM image (30×30 nm$^2$, 1.2 V/200 pA) of the A-type termination. The unit cell is labeled in the inset. (b) and (c) The (4×1) RHEED patterns along [001] and [110] directions with the integer diffraction spots indicated with the arrows, respectively.

![Figure 3](image3.png)  
**FIG. 3.** (Color online) (a) An STM image (16×16 nm$^2$, 1.2 V/20 pA) of the B-type termination. The unit cell is labeled in the inset. (b) An high-bias STM image (100×100 nm$^2$, 3.5 V/20 pA) of the B-type termination. The absorbed clusters form a (6×8) superstructure as illustrated in the inset. (c) and (d) The RHEED patterns along [001] and [110] directions with the integer diffraction spots indicated with the arrows, respectively.

![Figure 4](image4.png)  
**FIG. 4.** (Color online) (a) $S_A$ of the SrTiO$_3$(110) surface with different repeated cycles of cleaning (500 eV sputtering followed by UHV annealing at 1000 °C for 1 h). The sputtering dose is fixed for each series of cleaning cycles, while different dose is compared in different curves as labeled. The statistics are done over eight STM images (500×500 nm$^2$) for each data point. (b) $S_A$ with different Ar$^+$ sputtering dose. The ranges corresponding to different surface terminations are labeled.
cycle. Figure 4(b) reveals that the $S_A$ decreases from 1 to 0 linearly with the sputtering dose increasing. If the sputtering dose is too low, no atomically flat surface can be obtained (the “disordered” range in Fig. 4(b). There are windows of sputtering dose to get monophased surface with SrTiO and O terminations, respectively (the “A” or “B” range). Between the two windows, A- and B-type terminations coexist.

The annealing temperature and oxygen partial pressure are also changed from 800 to 1100 °C and from UHV to $6 \times 10^{-5}$ mbar, respectively. The structure of A- or B-type surface keeps stable without any other phase evolved. The statistical $S_A$ exhibits no obvious change either, while the domains of each type condensate respectively as the annealing temperature elevated. We do not observe any noticeable change of the $S_A$ with varied ion energies from 500 to 2000 eV at a fixed sputtering dose.

The termination of SrTiO$_3$(110) surface can also be tuned by epitaxially growing submonolayer amount of Sr or Ti. The as-deposited Sr atoms show different morphology on the A- and B-type domains (not shown here), suggesting different chemical characteristics of the two terminations. After annealed in UHV at 800 °C, $S_A$ increases. In comparison, depositing Ti followed by annealing results in the enlargement of B-type domains. These results clearly indicate that tuning of the surface termination is a process driven by the chemical content. It is well-known that preferential sputtering effect may change the surface stoichiometry upon different dose. Annealing activates the diffusion of different elements, especially O, from the bulk to surface. Moreover, sputtering also changes the surface morphology and may affect such diffusions. Therefore thermodynamically stable phases, SrTiO and O terminations, are formed upon annealing, establishing the phase separation picture on the surface that is determined by the chemical content. This is why the $S_A$ value is determined by the sputtering dose in each cycle, instead of the accumulated dose for all the preceding annealing cycles. On the other hand, it is suggested that the densely adsorbed clusters on the O termination are Ti-rich, while those on the SrTiO termination are Sr-rich. The Ti-rich clusters are normally positively charged. They contribute to the polar compensation to the exposing (O$_2$)$_{24}$ layer and are responsible for the surface stabilization. The SrTiO termination is stabilized primarily by the (4 $\times$ 1) reconstruction that modifies the electronic structure and reduces the surface polarity, while those sparsely adsorbed Sr-rich clusters play a secondary role.

In summary, we have obtained SrTiO$_3$(110) polar surface terminated by SrTiO and O layers with sputtering and annealing treatments, and identified their spatial distribution with STM. By adjusting the sputtering parameters, we can tune their relative areal ratio reproducibly and continuously, until monophased surface is obtained with either SrTiO or O termination. The surface is stable under various oxygen partial pressure and temperature, providing us a flexible epitaxial growth template for further investigations of the controlled functionalities of artificial low-dimensional oxides through interface engineering.

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References