Unit-Cell by Unit-Cell Homoepitaxial Growth Using Atomically Flat $SrTiO_3(001)$ Substrates and Pulsed Laser Deposition *

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Using a combination of chemical etching and thermal annealing methods, we have obtained atomically flat TiO_2-terminated $SrTiO_3(001)$ with large terraces. The average width of the terrace is only determined by miscut angles. When we continuously grow tens of $SrTiO_3$ monolayers on such a surface under pulsed laser ablation deposition condition at 621°C, the growth proceeds in a layer-by-layer mode characterized by un-damped oscillations of the specular RHEED intensity. After the growth of 180 monolayers, the surface morphology is restored to the pre-growth condition with similarly large terraces after annealing in vacuum for only 30 min, indicating efficient mass transfer on TiO_2-terminated terraces.

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$SrTiO_3(001)$ have been widely used as substrates for growth of high-quality thin films of perovskite oxides such as high-T_c superconductors, ferroelectric materials, and colossal magneto-resistive materials. This is because $SrTiO_3$ is chemically and compositionally stable, and many perovskite oxides have the same lattice structure and similar lattice constants as those of $SrTiO_3$. As-received $SrTiO_3(001)$ substrates practically have very different surface morphology, partially due to mechanical polishing processes that are needed for fabrication of oriented substrates. By annealing an as-received $SrTiO_3(001)$ substrate at high enough temperature for a certain time, the surface can become large terraces with the average width determined only by the miscut angle. However it typically has both SrO-terminated and TiO_2-terminated terraces with more or less equal proportions. Since the surface properties of both the terminating terraces are different, the *intra*-layer and *inter*-layer mass transports are different on these two types of terraces under the same temperature, deposition condition, and ambient. This makes a mix-terminated surface undesirable for growth of high-quality crystalline films since the detailed balance between deposition and mass transport kinetics plays a key role. Instead, single-terminated $SrTiO_3(001)$ is much more suitable as substrates for subsequent epitaxy of perovskite oxides. Since a SrO-terminated terrace is chemically different from a TiO_2-terminated terrace, chemical treatments are expected to be effective in removing one type of terraces while leaving the other intact. Kawasaki and coworkers were the first to obtain a TiO_2-terminated $SrTiO_3(001)$ surface by using pH-controlled NH_4F-HF solutions.[1,2] The solutions can selectively etch more basic SrO terraces away. However, reproducing single-terminated surfaces using this method depends strongly on the pH value of the solution as well as the polishing prior to and the annealing procedure after etching treatment. Koster and coworkers later reported a different chemical treatment procedure that is more reproducible and simpler.[3,4] Instead of etching SrO terraces directly with an NH_4F-buffered HF (BHF) solution, those authors first transform SrO into a Sr-hydroxide complex, confined to the topmost surface, by reacting the mix-terminated surface with water. In this process the TiO_2 terraces remain intact. Since Sr-hydroxide is more reactive with acidic solutions than SrO, it is readily dissolved in BHF without forming undesirable pits. Combined with a subsequent thermal annealing at 950°C for 30 min to one hour, those authors were able to reproducibly obtain TiO_2-terminated $SrTiO_3(001)$ with a much weak dependence on the pH value.

We apply this combination of chemical/thermal treatment to as-received $SrTiO_3(001)$ substrates and subsequently grew hundreds of $SrTiO_3$ monolayers on the treated surface using a pulsed laser deposition method. From the atomic force microscopic (AFM) images and reflection high-energy electron diffraction (RHEED) measurement, we find that (1) without the chemical treatment as described by Koster and coworkers,[3] a thermal annealing treatment of as-received $SrTiO_3(001)$ alone at a typical growth temperature of 621°C, even after three hours, leaves the surface with small terraces of both the terminations for the reason that the step height can be both one

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unit cell high and 1/2 unit cell high; (2) when we treat as-received $SrTiO_3(001)$ with a combination of chemical etching and subsequent annealing at 950°C for a few hours, the surface (pre-growth) becomes singly terminated with TiO_2 terraces with average width determined only by the miscut angle and with very few structure defects; (3) using pulsed laser-ablation deposition method $SrTiO_3$ film grows layer-by-layer on the treated $SrTiO_3(001)$ surface at 621°C with a deposition rate of 0.05 ML/s; (4) after hundreds of $SrTiO_3$ monolayers are deposited, the post-growth surface takes less than 30 min to restore back to the morphology of the pre-growth surface at 621°C, characterized by large TiO_2-terminated terraces.

We treated these substrates using two different methods. One is thermal annealing alone in which an as-received $SrTiO_3(001)$ substrate is annealed at 621°C for three hours in a pulsed laser deposition chamber with an oxygen ambient of 3×10^{-6} Torr. The other is a combination of chemical etching and thermal annealing, which we refer to as the full treatment. In this case, the as-received $SrTiO_3(001)$ substrate is first ultrasonically soaked in deionized water for 10 min to allow SrO-terminated terraces on the topmost surface to react with water and to form Sr-hydroxide while chemically stable TiO_2-terminated terraces remain intact. The substrate is subsequently put into an NH_4F buffered HF solution for 30 s so that the Sr-hydroxides are dissolved, leaving only TiO_2-terminated terraces. The pH value of the NH_4F buffered HF solution is 5.5. After etching, the substrate is put into a quartz tube in a furnace, and is annealed at 950°C in a constant flow of oxygen at the atmospheric pressure for eight hours. After the treatment of one method or the other, we examine the surface morphology with a commercial atomic force microscope (AFM). The latter is a nanoscope operated in tapping mode.

On a fully-treated $SrTiO_3(001)$ substrate, we grow $SrTiO_3$ films using the pulsed laser deposition (PLD) method in a deposition chamber as described previously.[5,6] We use 308-nm optical pulses from a XeCl Excimer laser to ablate a stoichiometric $SrTiO_3$ target, and monitor the film growth process with a reflection high energy electron diffraction (RHEED) system. The ambient pressure in the deposition chamber during growth is about 1×10^{-7} Torr. The substrate temperature during growth is 621°C and is monitored directly with an optical pyrometer. To examine the efficiency of the post-growth annealing on a fully treated substrate, we anneal the post-growth surface at 621°C for 30 min, remove the sample from the chamber after it is cooled down to room temperature, and examine the surface morphology of the surface with the AFM.

The surface morphology of a typical as-received $SrTiO_3(001)$ substrate was imaged by AFM. As shown in Fig. 1, the surface consists of terraces, with mounts of multiple unit cells in height.

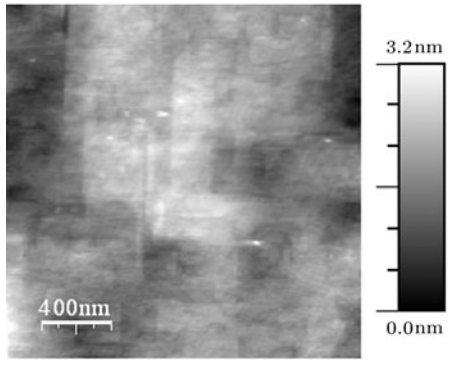

Fig. 1. AFM image over an area of 2 μm × 2 μm on an as-received $SrTiO_3$ (001) substrate. The surface consists of three-dimensional mounts of multiple unit cells in height.

Thermal annealing of an as-received $SrTiO_3(001)$ substrate at 621°C in an oxygen ambient of 3×10^{-6} Torr for three hours *alone* resulted in some re-growth of the surface. As shown in Fig. 2, the surface now consists of small shallow mounts of 2–3 unit cells in height and thus disordered step edges that are of either half unit cell (∼0.2 nm) or a single (∼0.4 nm) unit cell in height. The presence of a significant fraction of half-unit-cell high steps means that both SrO-terminated and TiO_2-terminated terraces are present on the surface. Even though the smoothness is improved, there are two chemically different terminations that are undesirable for subsequent epitaxial film growth on such a surface.

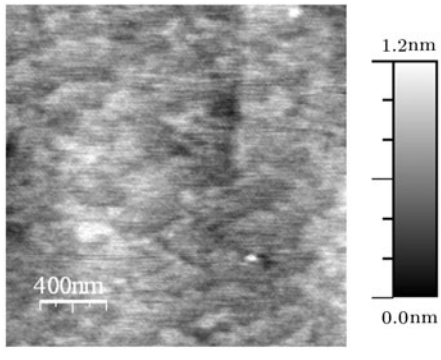

Fig. 2. AFM image over an area of 2 μm × 2 μm on a $SrTiO_3(001)$ substrate after it is thermally annealed in an oxygen ambient of 3×10^{-6} Torr at 621°C for three hours. The surface consists of small terraces and multiplayer mounts of 2–3 unit cells in height. Line scan along the surface shows that the step heights are either half (0.2 nm) or one (0.4 nm) unit cell in height.

Using a combination of chemical etching/thermal annealing method as described above, we obtained a singly terminated $SrTiO_3(001)$ surface as shown in Fig. 3. Wavy step edges separate wide terraces with the averaged width of 400 nm determined only by the miscut angle of the substrate. The line scan across the steps shows that the terraces are separated only

by 0.4 nm or one unit cell in height, indicating that the surface is terminated with one type of terraces. From chemistry of the etching treatment,[3,4] these terraces are TiO_2-terminated. Such a singly terminated atomically flat surface is an ideal substrate for controllable epitaxial film growth.

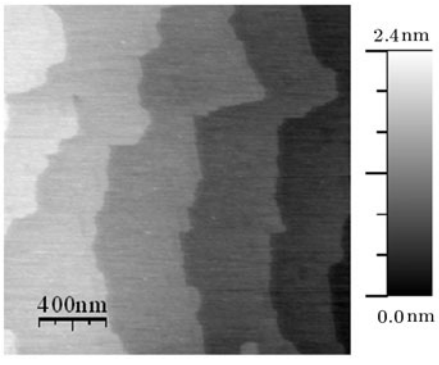

Fig. 3. AFM image over an area of $2\,\mu m \times 2\,\mu m$ on the surface of $SrTiO_3(001)$ as shown in Fig. 2, but after the full chemical/thermal treatment as described in the text. The line scan along the surface only shows steps that are 0.4 nm in height.

One benefit of having one termination on $SrTiO_3(001)$ surface is that we have only to deal with *intra*-layer and *inter*-layer mass transport across one crystalline surface plane and thus make it easy to understand and optimize subsequent epitaxial growth of perovskite oxides. Another benefit of having only TiO_2-terminated terraces is that the mass transport is more efficient on these terraces. As a result, it is easier to maintain the surface of an epitaxially grown $SrTiO_3$ film atomically flat. To demonstrate the advantage of a fully treated $SrTiO_3(001)$ surface for epitaxy, we performed a homoepitaxy experiment under the pulsed laser deposition condition. The substrate temperature during deposition was held at 621°C and the deposition was carried out in an oxygen-free ambient of 1×10^{-7} Torr. The morphology of the growth surface during deposition was monitored with the specular RHEED intensity. Figure 4 shows the RHEED intensity during the deposition of $SrTiO_3$ on a fully treated $SrTiO_3(001)$ surface. The strong undamped oscillations indicate a nearly perfect layer-by-layer epitaxial growth. During the pulsed laser ablation, nearly stoichiometric amounts of SrO and TiO_2 are deposited. One period in the RHEED intensity oscillations marks the completion of one unit cell growth that involves nominally the same portions of SrO and TiO_2.[7–10] Similar to what have been reported by Koster *et al.* and Eres *et al.*, the fact that one observes RHEED oscillations from such a growth surface only for completion of full monolayers (layers of one unit cell high) means that TiO_2 and SrO form unit cells first and rapidly, and $SrTiO_3$ unit cells then go through the processes of *intra*-layer and *inter*-layer mass transport, nucleation, growth, and finally coalescence.[3,11,12] Since nearly stoichiometric portions of SrO and TiO_2 are deposited by the pulsed laser ablation method, if the stoichiometry on the growth surface is not altered significantly by the difference in desorption kinetics for adsorbed strontium oxides and titanium oxides before they form relatively stable $SrTiO_3$ unit cells under the growth condition, we expect that the surface should more or less remain TiO_2-terminated after the growth of a film of $SrTiO_3$ on the fully treated $SrTiO_3(001)$. This is indeed the case. In Fig. 5, we show the AFM image of the fully treated $SrTiO_3(001)$ *after* 180 monolayers of $SrTiO_3$ were deposited. The image was taken after the deposited film was annealed further for 30 min in vacuum at the growth temperature of 621°C. It is remarkable that the surface morphology of the 180-monolayer-thick $SrTiO_3$ film resembles that of the starting substrate as shown in Fig. 3, with equally wide terraces and no 2D $SrTiO_3$ island or vacancy islands on top of them. The step height of 0.4 nm is exactly that of one unit cell. We note that under high oxygen pressures, other researchers have reported the appearance of SrO-terminated terraces on pulsed-laser-ablation deposited $SrTiO_3$ films on fully treated $SrTiO_3(001)$.[13] Our present results indicates that when the oxygen ambient pressure is low or even absent, the TiO_2-termination of a fully treated $SrTiO_3(001)$ remains after the deposition of a $SrTiO_3$ film under the pulsed laser deposition condition.[14]

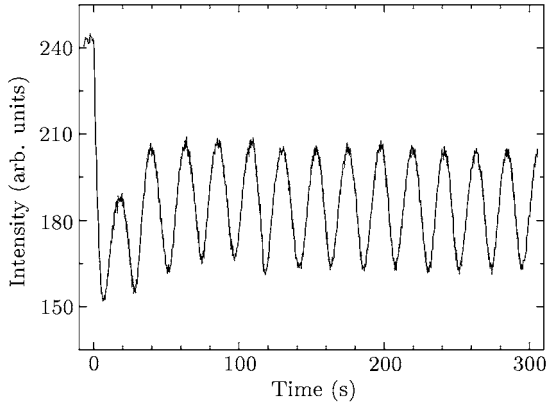

Fig. 4. Specular RHEED intensity from the growth surface during a pulsed laser deposition of $SrTiO_3$ on the fully treated $SrTiO_3$ (001) substrate. The strong and un-damped oscillations are indicative for a layer-by-layer growth.

It is informative to compare the surface morphology of a thermally annealed $SrTiO_3(001)$ without chemical etching treatment (Fig. 2) and the one shown in Fig. 5. Even after three hours of annealing at 621°C, the mixed terminated $SrTiO_3(001)$ surface is still covered with small 3-D islands of 2–3 unit cells high, instead of wide terraces as shown in Fig. 3. On the TiO_2

terminated surface, the ubiquitous islands of a few unit cells high after deposition of tens or hundreds of $SrTiO_3$ monolayers are removed or "flattened" in less than 30 min at 621°C, through the Oswald ripening in which the islands diminish to give ways to large terraces with large step curvature. This means that the mass transport of pulsed-laser-ablation deposited species on TiO_2-terminated terraces and the kinetics of Oswald ripening of TiO_2-terminated $SrTiO_3$ islands are much more efficient than those on a mixed terminated $SrTiO_3(001)$. This explains why on a $SrTiO_3(001)$ surface fully treated with a combination of chemical etching and thermal annealing, the growth of perovskite oxides tends to consistently yield sharp interfaces.[15]

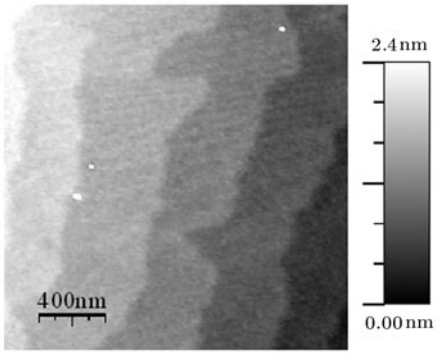

Fig. 5. AFM image over an area of 2 μm × 2 μm on the surface of a 180 unit-cell-thick $SrTiO_3$ film deposited on the fully treated $SrTiO_3$ (001) as shown in Fig. 3. The film is deposited with the pulsed laser ablation technique with the substrate temperature at 621°C. The film is subsequently annealed at 621°C for additional 30 min. The line scan along the surface again only shows steps that are 0.4 nm in height.

In summary, we have obtained nearly perfect TiO_2-terminated $SrTiO_3(001)$ by using a combination of chemical etching and thermal annealing, as suggested by Koster and co-workers.[3] The epitaxial growth of a $SrTiO_3$ film on such a fully treated surface proceeds layer-by-layer at 621°C under an oxygen-free vacuum. The morphology of the post-growth surface is *fully* restored to the pre-growth state after the annealing not more than 30 min at the growth temperature, indicating that Oswald ripening is more efficient on TiO_2-terminated $SrTiO_3(001)$ than on mixed terminated $SrTiO_3(001)$.

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