Atomically Resolved Surface Structure of SrTiO$_3$(001) Thin Films Grown in Step-Flow Mode by Pulsed Laser Deposition

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The surface structure of SrTiO$_3$(001) thin films homoepitaxially grown in step-flow mode by pulsed laser deposition was characterized using scanning tunneling microscopy. One-dimensional (1D) TiO$_2$-based nanostructures were formed on the surface, and their density increased with increasing film thickness. Most of the 1D nanostructures disappeared after post-deposition annealing, and the resulting surface exhibited a domain structure with (2 x 1) and (1 x 2) reconstructions and fewer oxygen vacancies. These results imply that the step-flow growth is likely to produce a TiO$_2$-rich surface and Ti deficiencies in the film, and that annealing can effectively reduce the density of atomic defects.

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Sr$_2$O$_3$ (SrTiO$_3$) has been the subject of considerable interest because of its huge potential in applications involving superconductivity$^1$, photocatalysis$^2$, ferroelectrics$^3$, quantum paraelectricity$^4$, and as a key material for oxide-based electronic devices$^5$. SrTiO$_3$ has attracted greater attention due to the recent discovery of metallic and magnetic interfaces between LaAlO$_3$ and SrTiO$_3$, two nonmagnetic perovskite insulators$^6,7$. In order to explore and design unique functionalities at these surfaces and interfaces, more attention should be paid to the electronic structure of the substrate and thin film surfaces at the atomic scale. To date, the surface quality of thin films during and after deposition has been characterized mainly by monitoring reflection high-energy electron diffraction (RHEED) oscillations and patterns, and an atomic-scale understanding of the surface structures of thin films has been still incomplete. In particular, it would be highly desirable to characterize surface structures associated with the growth process, in addition to local defects.

Scanning tunneling microscopy and spectroscopy (STM and STS) are ideal probes for this purpose. We have recently constructed a new STM with pulsed laser deposition (PLD) capability, which enables low-temperature STM/STS measurements of thin films without exposing their surfaces to air.

In this paper, we show the atomic-scale surface structure of SrTiO$_3$(001) thin films homoepitaxially grown in step-flow mode by PLD, and demonstrate that step-flow growth is likely to produce a TiO$_2$-rich surface and Ti deficiencies in the film. During post-deposition annealing, the rich TiO$_2$ diffused into the films to compensate for defects associated with Ti vacancies and oxygen vacancies, resulting in a stable surface structure with fewer oxygen vacancies.

The SrTiO$_3$(001) thin films were homoepitaxially grown on Nb-doped (0.1 at. %) SrTiO$_3$(001) substrates. The substrate surfaces were prepared by buffered HF etching$^8$ and subsequent annealing at 1000 °C for 0.5 h in a partial oxygen pressure $P_{O_2}$ of $\sim 1 \times 10^{-6}$ Torr. The substrate surface showed a clear step-and-terrace structure, but no atomically-ordered structure was observed.$^{10}$ Thin film growth was performed at 1100 °C in $P_{O_2}$ of $\sim 1 \times 10^{-6}$ Torr, and was monitored using RHEED. A KrF excimer laser ($\lambda = 248$ nm) with a repetition rate of 1 Hz was used, and the laser fluence at the target surface was $\sim 2.3$ J/cm$^2$. We prepared three samples, with thicknesses of 4 nm [10 unit cell (u.c.)], 14 nm (35 u.c.), and 40 nm (100 u.c.). Each film was grown on different substrate. After film growth, the samples were cooled to room temperature at a rate of $\sim 3$ K/s in $P_{O_2}$ of $\sim 1 \times 10^{-6}$ Torr, and transferred to the ultrahigh vacuum STM system Unisoku USM-1300S without exposing the surface to air. All STM measurements were performed at 78 K.

Figure 1(a) shows typical RHEED intensity oscillations during film growth, which exhibited exponential recovery to the initial intensity level, confirming the step-flow film growth mode. The RHEED pattern shown in Fig. 1(b) exhibits sharp streaks with Kikuchi lines, indicating the high quality of the thin film. The streaking between the specular and (01) spots corresponds to a (2 x 2) reconstruction. Figure 1(c) displays a wide-scale STM image of a 35 u.c. SrTiO$_3$(001) film, showing a clear step-and-terrace structure with a single unit cell step height ($\sim 0.4$ nm). The presence of such straight step edges is in distinct contrast to thin films grown in layer-by-layer mode, in which the step edges tend to be rather indented and small islands and pit structures exist on the terraces.$^{10}$

On a smaller scale, we observed characteristic one-dimensional (1D) nanostructures preferentially grown along the a or b crystallographic axis. We found that the density of these nanostructures increased with increasing film thickness [Figs. 1(d)–1(f)]. In the 10 u.c. film [Fig. 1(d)], only a few such nanostructures existed, and the surrounding surface exhibited a domain structure with a (2 x 1) and (1 x 2) reconstruction with many defects imaged as bright spots. The (2 x 2) streaks observed in the RHEED pattern were possibly due to this reconstruction. We note that a domain structure with (2 x 1) and (1 x 2) reconstructions has also been observed using high-resolution TEM in single-crystal SrTiO$_3$(001) prepared at 950–1000 °C with much higher oxygen pressure, and a complicated TiO$_2$-rich surface structure was proposed.$^{11}$ Therefore, a similar structure may have been formed in this 10 u.c. film. The defects observed in the (2 x 1) and (1 x 2) reconstructed surface were probably mainly oxygen vacancies, because the number of defects was substantially reduced by growing a 10 u.c. film under a higher oxygen pressure ($1 \times 10^{-5}$ Torr). A detailed discussion of these defects will be presented elsewhere.
As seen in Fig. 2(a), the surface of the thickest 100 u.c. film was completely covered with 1D nanostructures, clearly showing a (6 x 2) surface reconstruction in the fast Fourier transform (FFT) image [Fig. 2(b)]. A similar structure has been reported on a single-crystal surface prepared by sputtering and annealing, and was considered on the basis of Auger electron spectroscopy and STM measurements to be a TiO$_x$-based nanostructure growing on a TiO$_2$-rich surface.$^{[12]}$ X-ray diffraction (XRD) analysis of this film showed a c-axis expansion of only 0.001 nm, indicating that the film was nearly stoichiometric.$^{[13]}$ Therefore, despite the nearly stoichiometric films, increasing the film thickness resulted in the growth of more abundant Ti-related complexes on the surface, along with increased Ti deficiencies in the underlying film.

To investigate the effects of post-deposition annealing on this surface structure, the 100 u.c. film was further annealed for 1 h at 1100 °C in a $P_{O_2}$ of $\sim 1 \times 10^{-6}$ Torr. After annealing, the surface structure dramatically changed, as shown in Fig. 2(c). Most of the 1D nanostructures disappeared, and the surrounding surface exhibited randomly distributed (2 x 1) and (1 x 2) domains [Fig. 2(d)] with many defects, which was quite similar to the thinner 10 u.c. film [Fig. 1(d)]. This suggests that the 1D nanostructure is metastable, probably due to the highly nonequilibrium growth conditions.

To study the local electronic states in more detail, we performed STS measurements on the 10 u.c. film. The spectra were taken with a resolution of 128 x 128 pixels in a 25 nm x 25 nm region. The spectra from various surface locations can be divided into three categories: the 1D nanostructure, the surrounding (2 x 1) and (1 x 2) reconstructed surface away from defects, and defect sites [Fig. 3(a)]. The $dI/dV$ spectra taken at the 1D nanostructure and the (2 x 1) and (1 x 2) surface had similar line shapes and no apparent peak structure, but the defect regions (bright spots) showed characteristic peaks distributed over a wide energy range from 2.6 to 3.4 V. A representative $dI/dV$ spectrum with a peak structure is shown in Fig. 3(a). This suggests that the 1D nanostructure consisted of a similar stoichiometry to the surrounding (2 x 1) and (1 x 2) structures, in which many defects associated with oxygen vacancies were present.

In the annealed film, the $dI/dV$ spectra taken at defect regions showed similar peak structures. To perform a more detailed comparison with the 10 u.c. thin film, we plotted peak voltage probability distributions for the two films in Fig. 3(b). In the 10 u.c. film, the peak voltage was distributed over a wide range of $\sim 0.8$ V, with the most common value being $\sim 3.2$ V. In contrast, the annealed 100 u.c. film has

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**Fig. 1.** (a) RHEED oscillations during the homoepitaxial growth of SrTiO$_3$(001). (b) RHEED pattern of 10 u.c. SrTiO$_3$(001) thin film after growth. (c) Constant-current STM image of SrTiO$_3$(001) thin film (thickness: 35 u.c., 200 x 200 nm$^2$). Sample-bias-voltage $V_s = +2$ V, and a set-point tunneling current of $I_t = 40$ pA. (d)–(f) Thickness dependence of the surface structure of SrTiO$_3$(001) thin films (40 x 40 nm$^2$). $V_s = +2$ V, $I_t = 40$ pA. (d) 10 u.c. (e) 35 u.c. (f) 100 u.c.

**Fig. 2.** (a) STM image of a 100 u.c. SrTiO$_3$(001) film at $V_s = +1$ V, $I_t = 40$ pA, 13 x 13 nm$^2$. (b) FFT image corresponding to (a). (c) STM image of an annealed 100 u.c. SrTiO$_3$(001) film. $V_s = +1.5$ V, $I_t = 40$ pA, 25 x 25 nm$^2$. (d) Line profile along A–B and C–D in (c).
peaks in a relatively narrow range at higher voltages, and the defect density estimated from the STM images was lower, from $\sim 3.4 \times 10^{13} \text{ cm}^{-2}$ to $\sim 2.7 \times 10^{13} \text{ cm}^{-2}$, implying that the distribution of electronic states in the annealed film was more uniform than in the 10 u.c. film.

Taken together, these results provide a microscopic picture of the near-surface stoichiometry of thin films, depending on their thickness and post-deposition annealing as illustrated in Fig. 3(c). In the 10 u.c. film, a few 1D nanostructures and many local defects were observed on the (2 $\times$ 1) and (1 $\times$ 2) reconstructed surface, indicating the existence of a few Ti vacancies in the film and many oxygen vacancies at the surface. By increasing film thickness, the density of 1D nanostructures increased, suggesting increased TiO$_2$ on the surface and Ti vacancies in the film. After annealing, the TiO$_2$-based 1D nanostructures diffused into the underlying layer, and were incorporated into the Ti vacancies and oxygen vacancies. The most stable (2 $\times$ 1) and (1 $\times$ 2) reconstructed surface was formed with fewer oxygen vacancies. Additionally, we performed XRD measurements of 100 u.c. films before and after post-deposition annealing, but no clear difference was found between them. Therefore, the drastic annealing effect observed in STM images might occur only near the surface. However, we cannot rule out the possibility that the difference in stoichiometry between the two films was too small to be detected by XRD. The use of additional techniques with depth profile imaging capability, such as high-resolution TEM, should clarify this issue.

To date, most attempts to understand various interesting phenomena occurring at the oxide interface have been based on the concept of ideal surface termination. However, our results demonstrate that the surface structure of SrTiO$_3$ thin films is more complicated than that of the bulk crystal structure. The present results demonstrate that STM is a powerful tool for the characterization of the electronic structure of a wide variety of thin films on a truly atomic scale, and enables a new approach for the design of functional oxide films.

In conclusion, we performed the first investigation of the local surface structure of SrTiO$_3$ thin films using low-temperature STM. The surfaces of SrTiO$_3$(001) homoepitaxial thin films grown in step-flow mode with PLD exhibited TiO$_2$-based 1D nanostructures on a TiO$_2$-rich (2 $\times$ 1) and (1 $\times$ 2) reconstructed surface. Furthermore, the density of these nanostructures increased with increasing film thickness, indicating that the step-flow mode tended to produce a TiO$_2$-rich surface. During annealing, the metastable 1D nanostructures diffused into the subsurface, incorporating Ti vacancies and oxygen vacancies, and a (2 $\times$ 1) and (1 $\times$ 2) domain structure was formed at the surface with fewer defects. Our data suggests that post-deposition annealing can effectively provide electronically uniform thin film surfaces.

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