Growth and characterization of stable SrO-terminated SrTiO$_3$ surfaces

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A simple technique for the growth of SrO-terminated SrTiO$_3$ surfaces is reported. High quality SrTiO$_3$ epitaxial films were grown by reflection high energy electron diffraction assisted pulsed laser deposition on suitably prepared NdGaO$_3$ (110) substrates. The surface properties, analyzed within a growth/characterization multichamber ultrahigh vacuum system by photoemission spectroscopy performed on the core-level spectra of Sr and Ti, low energy electron diffraction-, scanning tunneling-, and atomic force microscopy, are fully consistent with a single Sr oxide termination. The availability of such high quality SrO-terminated SrTiO$_3$ surfaces is of major importance for the controlled growth of oxide epilayers and interfaces. © 2009 American Institute of Physics. [DOI: 10.1063/1.3052606]

The technology of epitaxial oxide film growth has been continuously progressing during the past decades, resulting in the capability to control structures, morphologies, surfaces, and interfaces at the highest level. It was soon realized that a prerequisite for achieving samples with a high degree of perfection is the availability of atomically smooth substrates. As a matter of fact, the demonstration of suitable procedures for obtaining SrTiO$_3$ (STO) crystals with flat single terminated (001) terraces contributed to the fortune of this material as a substrate for the growth of countless types of functional oxides. The STO lattice consists of an alternating stack of SrO (A-site) and TiO$_2$ (B-site) atomic layers along the [001] direction. In their pioneering work, Kasawaki et al. ¹ showed that a simple chemical etching can remove SrO at the STO surface so that a single TiO$_2$ terminating surface layer is obtained. Further improvements were achieved by the same authors and by others,²–⁵ demonstrating the feasibility of the TiO$_2$ termination with high crystallinity and straight step edges. A spectacular effect of the importance of surface termination is provided by the formation of a high mobility two-dimensional (2D) electron gas at the LaAlO$_3$/STO interface, which only takes place on B-site terminated STO.⁶

While control of the B-site termination of STO may be regarded nowadays as a standard protocol in many laboratories, the control over the A-site termination is by far more difficult. Such termination has been obtained by the deposition of a SrO monolayer onto a previously prepared B-site STO.⁷,⁸ The control of film thickness is achieved by monitoring reflection high energy electron diffraction (RHEED) during the growth and by calibrating the rate, with due care to achieve a complete layer¹⁰ while avoiding SrO precipitate formation. Only under very specific growth conditions (i.e., the so-called “interval deposition” technique) the surfaces of these samples are smooth,⁶ as demonstrated by atomic force microscopy (AFM) analyses, and well suited for successive layers growth.¹¹ We finally mention that there are routes to get the SrO termination of other perovskites; see, e.g., the work by G. Rijnders et al.,¹² who observed that the expected RuO$_2$ termination of SrRuO$_3$ deposited onto B-site STO was unstable due to the volatility of the ruthenium oxide.¹³

The A-site termination of STO is by far less investigated, in spite of the potential interest for catalytic processes¹⁴ and for the realization of specific functional heterostructures and interfaces making use, for example, of the dielectric or conducting (under electron doping) properties of STO. The main idea is that the terminating layer determines the stacking sequence in the heteroepitaxial growth of perovskites,¹⁵ according to the law that A- and B-sites are generally alternated. In principle, the properties of the deposited film may be sensitively affected by the interface properties through, e.g., charge transfer.¹⁶ In a recent work,¹⁷ some of the authors studied the crystallographic and morphological properties of both A- and B-site terminated STO single crystals, resorting to AFM, scanning tunneling microscopy (STM), and to grazing incidence x-ray diffraction. The results demonstrated the stability of the B-site termination against thermal treatments, also confirming the observation¹⁷ that SrO precipitates are formed during annealing. On the other hand, the nominally A-site terminated samples after long exposure to air appeared as not fully covered by SrO and more disordered probably due to a greater sensitivity of such surface to the interaction with the atmosphere.¹⁸

In the present letter, we show that a high quality SrO termination can be achieved by resorting to STO heteroepitaxial growth on (110) NdGaO$_3$ (NGO) substrates. This procedure has one fundamental advantage: the A-site termination of NGO is prepared through a thermodynamic equilibrium process, that is, a thermal treatment,¹⁹ which in our case was performed in a constant flow of pure oxygen at 1200 °C for 20 h. The crystal structure of NGO belongs to the space group $Pbnm$ with $a=0.543\,\text{nm},$ $b=0.550\,\text{nm},$ and $c=0.771\,\text{nm}$.20 It is deduced that a STO cell on (110) NGO has to match an effective in-plane rectangular lattice of 0.3867 × 0.3858 nm$^2$. The misfit with...
respect to the relaxed STO lattice parameter ($a_{STO}$ = 0.3905 nm) is therefore as small as 1.2%.

The experiments were carried out in our modular system for oxide deposition and analyses (MODA). MODA is a single multichamber ultrahigh vacuum (UHV) system including (i) a chamber (base pressure in the $10^{-9}$ mbar range) devoted to pulsed laser deposition (PLD) assisted by a RHEED operating up to 0.5 mbar O$_2$ and (ii) three analytical chambers (base pressure in the low $10^{-11}$ mbar range) equipped with UV photoemission spectroscopy/x-ray photoemission spectroscopy (UPS), spot profile analysis low energy electron diffraction (SPA-LEED), and AFM/STM. Before STO deposition, the NGO crystals were heated up to 800 °C in UHV. The AFM measurements (not shown) prove that this treatment yields very flat terraces with one termination. The RHEED image reported in Fig. 1(a), collected after introduction of 0.1 mbar O$_2$ in the chamber, demonstrates the high crystal quality of this surface. The PLD growth was performed by resorting to a 248 nm KrF-excimer laser, with typical fluence of $\sim$2.5 J cm$^{-2}$ at the target. STO deposition was carried out at 800 °C, 0.1 mbar of flowing O$_2$, and at a laser repetition rate in the range of 1–2 Hz. The sharp 2D-like diffraction patterns, collected at the end of depositions, confirm the excellent crystallinity, both in the case of thin films [Fig. 1(c)] and relatively thick films. The RHEED specular spot oscillations are regular [Fig. 1(b)]. The behavior is indicative of a growth that proceeds by nucleation and lateral expansion of grains. In a steady state regime, the delay between RHEED maxima indicates the time needed to complete a u.c. (unit cell) stack and hence the growth rate, which we varied in the range of 0.02–0.06 u.c./laser pulse. After interrupting the deposition, the RHEED signal increases, suggesting an ordering of the surface. The homoeptaxial growth of STO on such surface proceeds with improved regularity. As an example, the pattern in Fig. 1(d) shows oscillations that persist over more than 40 cycles.

After a brief annealing in vacuum at 800 °C needed to achieve a sufficient conductivity for measuring, the SPA-LEED patterns of the STO films deposited on (110) NGO show a sharp and clean signature of a (2 $\times$ 2) reconstruction [Fig. 1(e)]. This differs from the p(2 $\times$ 1) reconstruction, which is often observed in the case of STO single crystals with TiO$_2$ termination and has been ascribed to the ordering of oxygen vacancies.\textsuperscript{23} In situ noncontact AFM (NC-AFM) performed on as-grown samples [Fig. 2(a)] shows flat surfaces covered with islands, confirming that STO grows by 2D nucleation. Strikingly, the annealing in UHV (800 °C in $10^{-10}$ mbar for 75 min) of air-exposed samples [Fig. 2(b)] preserves the terrace smoothness and the step height of 0.39 nm (i.e., 1 u.c.). Even very thin STO films (6 u.c.) are very stable against annealing in different environmental conditions, including high oxygen pressures (up to 1 mbar) and high temperatures (800 °C) [Fig. 2(c)]. Each STM map was quantitatively analyzed. As a typical result, we show the height histogram in Fig. 2(d), revealing the occurrence of peaks separated by 0.39 nm. Both such data and the map morphology confirm that the samples have one termination, excluding half-cell steps at edges or at pits. It is worth mentioning that due to the high resolution of the STM technique, features corresponding to half-unit cell steps or less are easily detected on commercial STO single crystals processed at very high temperatures in UHV (>1000 °C).

Once the single termination of the surface is assessed, UPS was employed (a) to verify the chemical nature of the terminating layer (either TiO$_2$ or SrO) and (b) as a double check of full SrO coverage. UPS analyses were collected on an as-grown STO film deposited on NGO and on a TiO$_2$-terminated crystal (prepared as in Ref. 3) as a reference. The spectra of the $3d_{5/2}-3d_{3/2}$ Sr emission (Fig. 3) are normalized to the intensity of the corresponding $2p_{3/2}-2p_{1/2}$ Sr peak.

![Figure 1](image1.png)

**FIG. 1.** (Color online) High pressure RHEED images at 800 °C of (a) the (110) NGO surface before film deposition and of (c) 7 u.c. STO film (final). The RHEED oscillations of the specular reflection during the growth are in (b) and during subsequent STO homoeptaxy in (d). The SPA-LEED map in (e) shows the $(2 \times 2)$ reconstruction after annealing at 800 °C in UHV.

![Figure 2](image2.png)

**FIG. 2.** (Color online) Morphology of an 18 nm STO film. (a) In situ NC-AFM of the as-grown sample, showing $\sim$15% islands coverage. (b) STM after air exposure followed by thermal treatment at 800 °C in UHV. (c) NC-AFM on a 6 u.c. STO after overnight annealing at 800 °C in 0.1 mbar O$_2$. The histogram (d) shows 0.39 nm high steps only.

![Figure 3](image3.png)

**FIG. 3.** (Color online) Spectra of the $3d_{5/2}-3d_{3/2}$ Sr emission normalized to the intensity of the $2p_{3/2}-2p_{1/2}$ Ti peak. (a) STO film on NGO, normal vs shallow emission angle. (b) TiO$_2$-terminated STO crystal, normal vs shallow emission angle. (c) Comparison between the two (normal emission angle).
Ti peak. In Figs. 3(a) and 3(b), we show spectra of electrons emitted at normal and at shallow angle (35° to the surface), the latter being more sensitive to the surface chemical composition because of the short mean free path of the photoelectrons; the spectra at normal emission are compared in Fig. 3(c). The spectrum of normal-emitted photoelectrons is more intense in the case of the TiO2-terminated crystal. The opposite happens for the STO film, as expected for different crystallographic terminations. We also mention that the spectra of our STO homoepitaxial films grown on TiO2-terminated crystals (not reported) closely resemble those of the substrate.22 The experimental value of the intensity ratio of 3d Sr/2p Ti peaks can be compared with the corresponding theoretical value obtained for a perfect stacking of alternate A-B-A-⋯ layers, with no adjustable parameter.23 The results (normal emission: theory, 1.32; experiment, 1.3 ± 0.1; shallow angle: theory, 1.52; experiment, 1.5 ± 0.1) fully support our claim that a complete SrO layer terminates STO films on NGO.

It is worth mentioning that NGO is typically a much more perfect crystal than STO is, as also confirmed by our preliminary structural characterization by synchrotron light. It has been shown that STO films grown on substrates with a comparable degree of perfection, such as perovskitic scandates,24 even exceed the quality of commercial STO comparable degree of perfection, such as perovskitic.

The reported preparation method for a SrO-terminated NGO substrates by PLD assisted growth does not mean, however, that the physics of the reported growth mechanism can also be in-\(1\)voked in order to explain the presence of islands on the surface, which tend to get coarser during the growth process, in agreement with the following observations. First, \textit{in situ} AFM and STM measurements demonstrate that the growth on NGO is a self-controlled process. Also, the different reactivity of NGO and NGO surfaces with water is just the opposite happens for the STO film, as expected for different crystallographic terminations.

The reported data strongly support our initial guess that a single, A-site (i.e., SrO), termination is obtained. This statement is based on the following observations. First, \textit{in situ} AFM and STM measurements demonstrate steps with integer unit cell height and smooth terraces. Second, the chemical composition of the surface layer determined by XPS confirms that the terminating layer is SrO. Therefore, the STO films grow on NGO keeping the stacking sequence \(\cdots A-B-A-B-\cdots\) through the interface. Finally, the LEED indicates that the SrO surface has a high crystallinity and, after UV annealing, a peculiar \(c(2 \times 2)\) reconstruction, thus indicating that a well ordered surface lattice is realized, and that such a structure is stable, as \textit{ab initio} calculations anticipate.25 This termination is also perfectly suitable for successive growth process, as demonstrated by our data of STO homoepitaxy, which is characterized by a coherent growth with large RHEED oscillations over tens of unit layers.

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