

Ti- and Sr-rich surfaces of SrTiO₃ studied by grazing incidence x-ray diffraction

A. Fragneto, G. M. De Luca, R. Di Capua, U. Scotti di Uccio,^{a)} and M. Salluzzo^{b)}
CNR-INFM Coherentia, Complesso Monte S. Angelo, via Cinthia, 80126 Napoli, Italy

X. Torrelles

Institut de Ciència de Materials de Barcelona (CSIC) Campus de la UAB, Bellaterra, 081893 Barcelona, Spain

Tien-Lin Lee and J. Zegenhagen

European Synchrotron Radiation Facility, 6 Rue Jules Horowitz, BP 220, F-38043 Grenoble, France

(Received 25 May 2007; accepted 15 August 2007; published online 7 September 2007)

The structure of SrTiO₃ (100) (STO) single crystal surfaces has been investigated by grazing incidence x-ray diffraction. The authors found that chemically etched STO is composed ~75% of an ideal TiO₂ surface layer and ~25% of SrO and it is very stable when annealed in ultrahigh vacuum or in O₂ at high temperatures. A monolayer of SrO, epitaxially grown by pulsed laser deposition, is found to cover only a fraction of the TiO₂ layers and exhibits a 2 × 2 reconstruction with strong structural changes after annealing in conditions typically used for the deposition of oxides. © 2007 American Institute of Physics. [DOI: 10.1063/1.2779972]

SrTiO₃ (STO) is the most popular substrate for epitaxial growth of perovskite films,¹ and it is widely employed as a functional layer in all-oxide devices, such as field effect transistors² and tunnel junctions. For these reasons, there is a tremendous interest in the study of its surface properties. After years of investigations, it is now clear that the nature of the STO surface is actually quite complex. Nominally, (100) STO has two possible terminations, i.e., the TiO₂ or the SrO plane. Starting from (100) polished surface, a Ti-rich termination is achieved either resorting to suitable chemical etching,^{3,4} or to annealing in UHV at high temperatures.⁵ Most of the experimental work was performed on these surfaces that show also different kinds of reconstructions depending on the surface conditions before the annealing procedure (for review, see Ref. 6 and references therein). Much more difficult is the creation of a complete, unreconstructed SrO monolayer. On the other hand, the SrO terminated STO (100) is of interest for the realization of different functional interfaces through the control of the stacking sequence in heteroepitaxial growth.

For the growth of oxides, STO single crystals are heated up to several hundreds of degrees in an oxidant atmosphere. There is poor knowledge of possible surface structural and compositional changes during this process. In this letter we report a comparison between the structures of nominal TiO₂ and SrO terminated STO (100) surfaces after annealing in oxygen. After this treatment, STO is insulating and consequently low energy electron diffraction and scanning tunneling microscopy cannot be used for structure determination. For this purpose, we employed grazing incidence x-ray diffraction (GIXD) technique, using synchrotron radiation. The surface termination was adjusted by a combination of chemical etching and pulsed laser deposition (PLD). The STO (100) single crystals, with a miscut of less than 0.1° along the (100) direction, have been supplied by Twente Solid

State Technology BV. A TiO₂ termination is created by chemical etching and annealing at 950 °C in flowing oxygen, according to the procedure described in Ref. 4. After this process, the surface shows very well ordered terraces with single unit cell steps. Shear force microscopy, performed in air, did not show any contrast on a single terrace. This is generally considered a sufficient demonstration of a single termination. However, noncontact atomic force microscopy (NC-AFM), performed in ultrahigh vacuum (UHV) by Omicron VT-AFM system, shows islands half a unit cell high and few nanometer wide, randomly distributed on the terraces [Fig. 1(a)]. This may indicate that a minor part of the surface is SrO terminated. A nominal SrO surface is created by depositing a monolayer of SrO on top of the TiO₂ terminated STO by reflection high energy electron diffraction

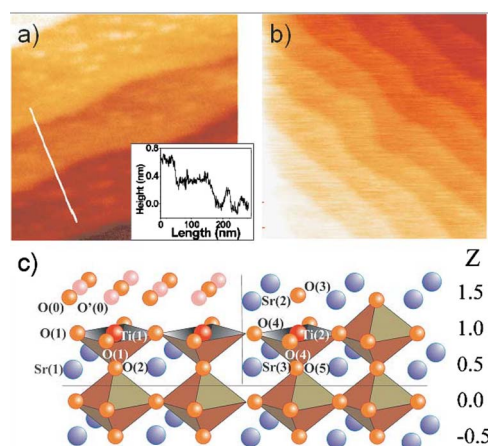


FIG. 1. (Color online) (a) NC-AFM in UHV (500 × 500 nm²) and height cross section showing the presence of small islands 0.2 nm high on the top of nominal TiO₂ terminated STO(100) surface. (b) AFM image (2 × 2 μm², contact mode in air) of nominal SrO terminated STO(100) surfaces. (c) Surface structural model used to fit the experimental GIXD data using the ROD program consisting of a mixed terminated TiO₂ (on the left side) and SrO (on the right side) surfaces. The labels for the atoms correspond to the ones used to identify them in Table II. An oxygen overlayer covering the TiO₂ layer and composed by two different sublattices [O(0) and O'(0)] is also considered.

^{a)}Also at DiMSAT, Università di Cassino, via Di Biase 43, 03043 Cassino (FR) Italy.

^{b)}Author to whom correspondence should be addressed; electronic mail: salluzzo@na.infn.it

TABLE I. Schematic description of the five surfaces studied and of the preparation methods: (a) Chemically etched and annealed in furnace at 950 °C in flowing O₂, (b) T1, plus UHV annealing at 900 °C, (c) T1, plus annealing in 0.1 mbar of flowing O₂ at 700 °C, (d) film deposition by PLD on a T1 surface, are (e) S1, plus annealing in 0.1 mbar of flowing O₂ at 700 °C. In the last two columns, the reduced χ^2 from the final refined model, model II, is shown.

	Termination (nominal)	Preparation method	Surface lattice	χ^2
T1	TiO ₂	(a)	1 × 1	1.3
T2	TiO ₂	(b)	1 × 1	1.3
T3	TiO ₂	(c)	2 × 2	2.2
S1	SrO	(d)	1 × 1	1.3
S2	SrO	(e)	2 × 2	1.2

(RHEED) assisted pulsed laser deposition.⁴ The deposition is stopped when the specular RHEED intensity reaches the first maximum. The resulting surface shows steps of one unit cell height as well [Fig. 1(b)]. However, each terrace exhibits a rms roughness of about 0.2 nm, which may indicate partial exposure of other layers and thus an incomplete, but uniform, SrO coverage.

The surface preparation and GIXD experiment were performed at the surface-diffraction ID32 beamline of the European Synchrotron Radiation Facility. Samples T1 and S1, respectively, etched and covered by SrO (see Table I) were transported through air prior to being introduced into a small UHV “baby chamber” at base pressure of 10⁻¹⁰ mbar. The energy and incidence angle of the incoming x-ray beam was set to 15 keV and 0.25° (slightly higher than the critical angle), respectively. Crystal orientation was achieved through 24 Bragg STO reference reflections. Crystal truncation rods (CTRs) were collected by subsequent acquisition of rocking scans, i.e., by rotating the sample around the axis perpendicular to its surface at different L values [spacing 0.05 reciprocal lattice units] for fixed (H , K) values. In total, six nonequivalent CTRs were recorded for each sample. Finally, the possible presence of reconstructions was checked by scans along different H and K directions (at small L values) in reciprocal space.

We studied five surfaces, three of them expected to be TiO₂ terminated, and the other two expected to be SrO terminated (see Table I). Surfaces T3 and S2 were created by annealing T1 and S1 in 0.1 mbar of flowing O₂ at 700 °C. These are typical conditions for the growth of oxides on STO single crystals. Only these surfaces are reconstructed and both of them exhibit a 2 × 2 lattice.

The calculations of the CTR intensities have been performed using a modified version of the ROD software.⁷ Recent complex models derived from GIXD measurements⁸ and characterized by a double TiO₂ layer at the surface only provide a poor fit to our data ($\chi^2 > 3.2$, agreement factor $R > 0.3$). On the other hand, we find similarities with data reported in Refs. 9 and 10. After many attempts with a large number of possible structures, we have found that a surface composed of two different terminations is the only one able to reproduce the data [Fig. 1(c)]. Starting from the interface with vacuum, we consider (i) a 1 × 1 TiO₂ terminated STO unit cell covered by a disordered oxygen layer composed by two oxygen sublattices [O(0) and O'(0)] with equal population¹¹ and (ii) a 1 × 1 STO TiO₂ surface having an additional SrO monolayer on the top. Both types of terraces are considered coherent, corresponding to a representation of

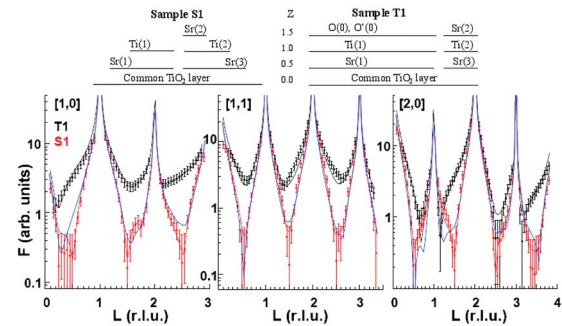


FIG. 2. (Color online) Comparison between the nominal TiO₂ terminated T1 (black symbols) and SrO terminated S1 (red symbols) surfaces for selected CTRs. The continuous lines are theoretical fits to model II. For S1 the blue curve is a fit using model I. On the top of the figures a simple sketch of the distribution of the layers as a result of the structural refinement is shown for S1 (on the left) and T1 (on the right) samples.

a surface where both types of terminations are distributed without any particular order. The model is completed by the addition of one unit cell to the structure, common to the two surface terminations. The TiO₂ termination is composed of two layers, Ti(1) and Sr(1), while the SrO one consists of three, i.e., Sr(2), Ti(2), and Sr(3). The relative ratio between the two surfaces is a fitting parameter of the model, together with 19 parameters for the Z displacements (cation and oxygen are considered separately), plus one Debye-Waller coefficient for each surface termination, a scaling factor, and a roughness parameter. An average reduced χ^2 for all data sets of about 2 or less is obtained, while single terminated models do not give a χ^2 value lower than 4. In particular, data on T1, T2, and T3 are nicely reproduced, while some details in the CTRs of S1 and S2 are not followed by the fit, as shown in Fig. 2, in the case of the S1 sample (blue line). For this reason, we have considered the possible presence of disorder on the surface, by adding five occupancy parameters for the layers composing each termination (oxygen and cation occupancies are forced to be identical due to the lower scattering strength of oxygen atoms). It turns out that a reduced χ^2 of the order of 1.3 (agreement factor $R < 0.12$) is obtained for each data set (see Table I). The very good agreement between the data and the fitted curves can be noted in Fig. 2 for S1 and T1 samples and in Fig. 3 for the treated T2, T3, and S2 samples.

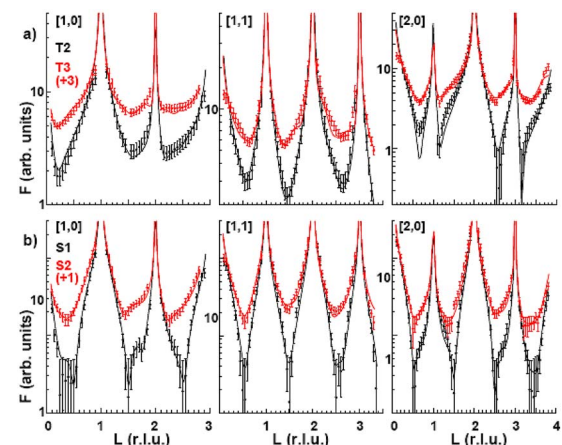


FIG. 3. (Color online) Experimental CTRs and fitted curves according to model II (continuous lines) on a logarithmic scale. (a) Samples T2 (black) and T3 (red) and (b) samples S1 (black) and S2 (red). The black and red curves are shifted one unity, as indicated in the figure, for clarity.

TABLE II. Relative ratio SrO:TiO₂ (in percent) between the topmost surface layers and surface normal displacements of atoms from the bulk positions [see Fig. 1(c)] given normalized to the STO lattice constant (in relative units). The average error bar is ± 0.004 with exception of some oxygen ions marked with a star, where the error can be as large as 50% mainly due to the low occupancy. T1, T2, and T3 samples have an additional disordered oxygen overlayer, 50% occupied as indicated in the text. In S1 and S2, a 100% surface occupancy is achieved in four atomic levels instead of two. The numbers in brackets are then the fraction of layers exposed following the sequence Sr(2):Ti(1)+Ti(2):Sr(1)+Sr(3): common TiO₂ layer.

Sample	T1 ($\Delta Z/a_0$)	T2 ($\Delta Z/a_0$)	T3 ($\Delta Z/a_0$)	S1 ($\Delta Z/a_0$)	S2 ($\Delta Z/a_0$)
	[18:35:19:28]	[23:56:9:12]
SrO:TiO ₂ (%)	30:70	24:76	33:66	37:63	32:68
Ti(1)	+0.006	-0.015	-0.006	-0.007	0.007
O(1)	+0.008	-0.009	-0.095	+0.007	+0.020*
Sr(1)	+0.005	-0.009	-0.003	+0.002	0.0
O(2)	+0.007	+0.022	+0.099	+0.025	-0.020
Sr(2)	+0.070	+0.011	+0.022	-0.011	+0.009
O(3)	+0.075*	-0.060*	+0.050*	-0.012*	+0.025*
Ti(2)	-0.015	-0.009	+0.052	+0.016	+0.014
O(4)	-0.020*	-0.010	-0.095	+0.008	-0.015
Sr(3)	-0.013	-0.002	+0.016	-0.010	-0.035
O(5)	-0.016*	-0.045*	+0.099	-0.020*	-0.025*

In Table II the main results of our experiment are summarized. Samples T1, T2, and T3 show a rather high TiO₂/SrO surface termination ratios of about 4:1, showing a terrace distribution involving two layers, i.e., the surface is about 25% covered by the Sr(1) layer and 75% by Ti(1). In these samples, a disordered oxygen overlayer covering the TiO₂ termination, as described in the model, gives a slight better fit of the data. Samples S1 and S2 show different trends. The oxygen overlayer on top of the TiO₂ regions is not present, while up to four layers, with different proportions, are exposed at the interface with vacuum as sketched in Fig. 2. For example, S1 is quite disordered and is composed of different layers, i.e., by 18% of Sr(2), 35% of Ti(1) plus Ti(2), 19% of Sr(1) plus Sr(3), and 28% of the bulk like TiO₂ layer below. Unexpectedly, the ratio between SrO and TiO₂ surfaces is 2:3 (~40% of the surface has a SrO layer exposed while the other 60% is TiO₂). At the same time and in a general way, atomic displacements, summarized in Table II, are very small in the case of the TiO₂ terminated surfaces while they are relatively large for the SrO one.

After treatment by high temperature annealing in oxygen and in UHV, T3 and especially T2 are found to be very similar to T1 (see Table II and Fig. 3). The ratio between TiO₂ and SrO termination changes only slightly among the samples, while minor changes in the ion displacements, as shown in Table II, are observed. On the contrary, strong differences in the CTRs [Fig. 3(b)] and thus in the surface structures and relative ratio between SrO and TiO₂ exposed layers are seen between S1 and S2, i.e., in the nominal SrO terminated surface after annealing in 0.1 mbar of oxygen. In particular, S2 shows also quite different displacements both in the SrO fraction and in the TiO₂ layers, but of the same order of magnitude of T2 and T3 samples compared to T1.

There are several interesting outcomes of our experiment. First, we found that a chemically etched STO surface shows ~20%–30% of SrO islands on the top of a TiO₂ layer, randomly distributed as x-ray results suggest. This is in qualitative agreement with NC-AFM data and with the investigation reported in Refs. 12 and 13, where it was demonstrated that SrO is formed during thermal treatment in oxygen. We also found that a deposited monolayer of SrO only covers a fraction of this surface and is quite disordered. We can envisage at present two possible explanations for this result: (a) the SrO monolayer is not stable, so that when exposed to air it partially reacts with carbon and water forming amorphous Sr hydroxide complex and (b) SrO actually grows by forming small two-dimensional islands that do not coalesce; consequently, even at the maximum of the RHEED intensity, this surface is not fully covered, but it is instead in a condition of minimum roughness.

In conclusion, we have studied the surface structure of nominally TiO₂ and SrO terminated SrTiO₃ (100) single crystals and their stability and structure relaxation after annealing. We demonstrate that a predominantly TiO₂ terminated surface, obtained by chemical etching, is quite stable, while after SrO deposition the surface is not fully covered, more disordered, and unstable. A relatively simple model describes the STO structure, partially intuitively understandable. These results have implications for the realization of devices, since suitable treatments can lead to almost unrelaxed substrate surfaces for interface engineering, possibly useful for the development of fully oxide electronics.

The authors are grateful to Guus J. H. M. Rijnders, F. Miletto Granozio, and M. Radovic for discussion. The authors thank C. Damen (TSST BV) for providing the high quality samples. Two of the authors (M.S. and G.M.D.L.) acknowledge the support from EU under Project Nanoxide Contract No. 033191. Another author (X.T.) thanks M.E.y.C. for its support through Project No. MAT2005-01736.

- ¹J. S. Speck, D. K. Fork, R. M. Wolf, and T. Shiosaki, *Mater. Res. Soc. Symp. Proc.* **401**, 1 (1996).
- ²X. X. Xi, Q. Li, C. Dougherty, C. Kwon, S. Bhattacharya, A. T. Findikoglu, and T. Venkatesan, *Appl. Phys. Lett.* **59**, 3470 (1991).
- ³M. Kawasaki, K. Takahashi, T. Maeda, R. Tsuchiya, M. Shinohara, O. Ishiyama, T. Yonezawa, M. Yoshimoto, and H. Koinuma, *Science* **266**, 1540 (1994).
- ⁴G. Koster, B. L. Kropman, G. J. H. M. Rijnders, D. H. A. Blank, and H. Rogalla, *Appl. Phys. Lett.* **73**, 2920 (1998).
- ⁵Q. D. Jiang and J. Zegenhagen, *Surf. Sci.* **425**, 343 (1999).
- ⁶I. Joumard, X. Torrelles, Tien-Lin Lee, O. Bikondoa, J. Rius, and J. Zegenhagen, *Phys. Rev. B* **74**, 205411 (2006).
- ⁷E. Vlieg, *J. Appl. Crystallogr.* **33**, 401 (2000).
- ⁸R. Herger, P. R. Willmott, O. Bunk, C. M. Schlepütz, B. D. Patterson, and B. Delley, *Phys. Rev. Lett.* **98**, 076102 (2007).
- ⁹G. Charlton, S. Brennan, C. A. Muryn, R. McGrath, D. Norman, T. S. Turner, and G. Thornton, *Surf. Sci. Lett.* **457**, L376 (2000).
- ¹⁰V. Vonk, S. Konings, G. J. van Hummel, S. Harkema, and H. Graafsma, *Surf. Sci.* **595**, 183 (2005).
- ¹¹This disordered layer is equivalent to an oxygen overlayer as that proposed by Vonk *et al.* in Ref. 10 but with oxygen occupancy of 50% in each site. In this way, unphysical short distances between oxygen atoms are avoided.
- ¹²T. Ohnishi, K. Shibuya, M. Lippmaa, D. Kobayashi, H. Kumigashira, M. Oshima, and H. Koinuma, *Appl. Phys. Lett.* **85**, 272 (2004).
- ¹³D. Kobayashi, R. Hashimoto, A. Chikamatsu, H. Kumigashira, M. Oshima, T. Ohnishi, M. Lippmaa, K. Ono, M. Kawasaki, and H. Koinuma, *J. Electron Spectrosc. Relat. Phenom.* **144-147**, 443 (2005).