

## Quest for a pristine unreconstructed SrTiO<sub>3</sub>(001) surface: An atomically resolved study via noncontact atomic force microscopy

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The surfaces of perovskite oxides affect their functional properties, and while a bulk-truncated  $(1 \times 1)$  termination is generally assumed, its existence and stability is controversial. Here, such a surface is created by cleaving the prototypical SrTiO<sub>3</sub>(001) in ultrahigh vacuum, and its response to thermal annealing is observed. Atomically resolved noncontact atomic force microscopy (nc-AFM) shows that intrinsic point defects on the as-cleaved surface migrate at temperatures above 200 °C. At 400 °C–500 °C, a disordered surface layer forms, albeit still with a  $(1 \times 1)$  pattern in low-energy electron diffraction (LEED). Purely TiO<sub>2</sub>-terminated surfaces, prepared by wet-chemical treatment, are also disordered despite their  $(1 \times 1)$  periodicity in LEED.

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Materials crystallizing in the perovskite structure attract attention in many fields due to their high tunability and the resulting, broad spectrum of physical and chemical properties [1–3]. Most applications of these materials rely on their surfaces and interfaces. The nonbinary chemical composition of perovskites allows for many different surface terminations [4–7] with dramatically different chemical and physical behaviors. It is mostly assumed, however, that perovskites prepared by wet chemical techniques are bulk-terminated  $(1 \times 1)$  [8]. Theoretical modeling of catalytic processes [9,10] and physical phenomena [11,12] generally assume this pristine surface structure. The interfaces between two perovskites preserve the bulk crystal structure and the properties of the junction are strongly influenced by the local defect chemistry. Several emerging applications could also profit from the bulk termination, such as employing ferroelectricity for optimizing or promoting catalytic reactions [13,14].

Surprisingly, the available atomic-scale information on bulk-terminated cubic perovskites is quite limited. A prototypical example is SrTiO<sub>3</sub>: the most common SrTiO<sub>3</sub>(001) surface preparation method is wet-chemical treatment. Etching with buffered-HF [8] preferentially removes the SrO layer and leaves the surface fully covered with flat, TiO<sub>2</sub>-terminated terraces [15,16]. This method was re-examined several times [17–21]; as was shown by x-ray photoelectron spectroscopy (XPS) it can induce an unintentional substitution of oxygen with F [22]. This can be avoided by etching the surface with HCl–HNO<sub>3</sub> [23] or nonacidic solvents [22,24,25]. Etched

surfaces must undergo annealing to at least 600 °C after introduction into vacuum to remove adsorbates. Up to this temperature, perfectly flat, TiO<sub>2</sub>-terminated surfaces usually display a  $(1 \times 1)$  pattern in low-energy electron diffraction (LEED) or reflection high-energy electron diffraction (RHEED) [18,26], while a series of surface reconstructions appear after annealing at higher temperatures [19,21,27,28]. Some reconstructions were atomically resolved using scanning tunneling microscopy (STM) including the  $(1 \times 2)$ ,  $(2 \times 2)$ ,  $c(4 \times 2)$ ,  $c(4 \times 4)$ , and  $c(6 \times 2)$  [7,18,25,29,30], and several more on surfaces that were sputtered and annealed in ultrahigh vacuum (UHV) [17].

So far, the structural characterization of SrTiO<sub>3</sub>(001) and other cubic perovskites was mostly based on diffraction techniques. A simple  $(1 \times 1)$  diffraction pattern could also stem from the bulk underneath a disordered layer, however; a true proof of a crystalline top surface requires atomically resolved imaging. For perovskite oxides this has been demonstrated only recently [31,32] using noncontact atomic force microscopy (nc-AFM, AFM hereafter) [33]. This technique provides clear, atomically resolved images of the  $(1 \times 1)$  termination, whereas STM shows no atomic corrugation [31]. It should be noted that the cleaving process that produces such unequivocally crystalline  $(1 \times 1)$  terminated SrTiO<sub>3</sub>(001) surfaces relies on incipient ferroelectricity, and that the induced polarity necessarily results in a sizable density of charged point defects [31]. Such cleaved surfaces can have micron-sized domains with exclusively TiO<sub>2</sub> and SrO termination, and each contains  $14 \pm 2\%$  Sr adatoms and Sr vacancies, respectively.

One could expect that thermal annealing heals such intrinsic point defects. Instead, this work shows that the as-cleaved SrTiO<sub>3</sub>(001)- $(1 \times 1)$  surface is unstable. Raising the temperature results in the lateral migration of the point defects, and an overlayer without long-range order forms above 400 °C. Having established that AFM is capable of providing a clear

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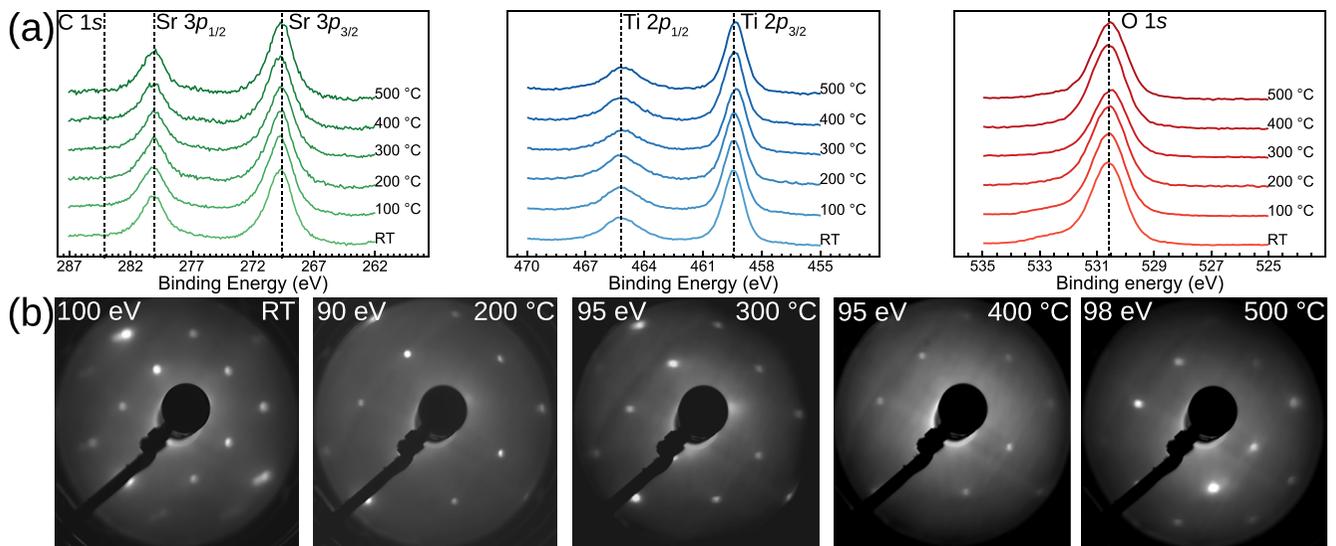


FIG. 1.  $\text{SrTiO}_3(001)-(1 \times 1)$ , cleaved at room temperature and annealed to increasing temperatures. (a) XPS spectra of the main core levels, obtained with  $\text{Mg } K_\alpha$  radiation. Spectra are offset vertically for clarity. (b) LEED patterns recorded at room temperature after cleavage, and after various annealing steps. No substantial change is discerned in these area-averaging measurements.

picture of ordered perovskite surfaces, it was applied to  $\text{SrTiO}_3(001)$  prepared by wet etching. These samples show no signs of an ordered surface in AFM, however, raising doubts that the commonly observed  $(1 \times 1)$  diffraction pattern indicates a crystalline, unreconstructed surface.

$\text{SrTiO}_3$  samples doped with 0.7 at.% Nb were used. For cleaving, samples were held in a cleaving device [31] constructed from Mo. After insertion into a UHV chamber with a base pressure below  $2 \times 10^{-10}$  mbar, the device was thoroughly degassed at  $500^\circ\text{C}$  and cooled down to room temperature (RT) prior to cleaving. Annealing was performed *via* a resistive-heating wire below the sample mount. The precision of the reported annealing temperatures is estimated as  $\pm 30^\circ\text{C}$  due to the limited thermal conductivity of the sample mount. Annealing times ranged from 30 to 60 min.

Scanning-probe measurements were performed in UHV with a base pressure below  $2 \times 10^{-11}$  mbar on a ScientaOmicron low-temperature STM/AFM at either  $T = 77.7$  or  $4.8$  K, using qPlus cantilevers [34] with a separate wire for the tunneling current [35] and a differential preamplifier [36]. Etched tungsten tips were glued on the tuning fork and cleaned by self-sputtering in Ar atmosphere [37] prior to the experiment. The resonance frequency of the qPlus cantilevers ranged from 25 to 80 kHz, with Q factors of  $\approx 50000$ . The STM images were obtained by applying a positive bias to the sample. All presented AFM images were acquired with an oxygen-terminated tip [38], i.e., surface cations appear attractive (bright) and anions repulsive (dark) [39].

Figure 1 shows XPS and LEED results of the  $\text{SrTiO}_3(001)$  by *in situ* cleaving [31], and after annealing at increasingly higher temperatures for 45 min each, up to  $500^\circ\text{C}$ . In XPS, the surface spectra of the constituents do not change, indicating that the overall surface stoichiometry is preserved. Despite the reducing character of the UHV environment, the elements retain their oxidation state.

The as-cleaved surface exhibits a clear  $(1 \times 1)$  LEED pattern. The periodicity does not change after various annealing steps. On the other hand, the sharpness of the LEED spots and the background intensity vary: the sharpest diffraction pattern was observed after annealing at  $200^\circ\text{C}$ , while further annealing degraded the pattern somewhat. A distinct  $(1 \times 1)$  LEED pattern is also reported throughout literature for polished  $\text{SrTiO}_3(001)$  surfaces annealed at temperatures above  $600^\circ\text{C}$ , necessary for degassing after introduction into UHV. Above  $850^\circ\text{C}$ , spots originating from  $c(4 \times 2)$  [40,41], or  $(1 \times 2)$  [18] reconstructions start to appear.

The surfaces of cleaved samples have SrO and  $\text{TiO}_2$  domains that span 10 to  $100 \mu\text{m}$  [31]. This is below the resolution of either of the techniques applied in Fig. 1. The STM/AFM results in Figs. 2 and 3 show the temperature evolution of the two terminations separately.

Figure 2 focuses on the SrO termination. STM images illustrate the large-scale surface morphology, while smaller-size AFM images provide details of the atomic structure. After cleaving at room temperature the surface is atomically flat [31]. The SrO  $(1 \times 1)$  surface is covered with the specific concentration of  $14 \pm 2\%$  of Sr vacancies,  $\text{V}_{\text{Sr}}^{2-}$ , apparent as black, ‘missing’ atoms in Fig. 2(b) [31]. The corresponding STM image shows a corrugation as high as a full unit cell ( $\approx 0.4$  nm), which is a purely electronic effect originating from the band bending induced by the charged Sr vacancies.

Annealing at  $250^\circ\text{C}$  results in the formation of pits at the flat SrO terraces, seen in both, STM and AFM. Their surroundings remain unreconstructed, with fewer  $\text{V}_{\text{Sr}}^{2-}$  defects. Intrinsic  $\text{V}_{\text{Sr}}^{2-}$  agglomerate into larger half-unit-cell-deep pits, that expose the underlying  $\text{TiO}_2$  termination. No oxygen atoms are visible within the pits; they can be considered aggregates of Schottky-type defects [42], formed by Sr vacancy diffusion and the formation of O vacancies [43]. STM images of the SrO domains annealed to  $250^\circ\text{C}$  and  $330^\circ\text{C}$  show significantly smaller corrugation compared to the as-cleaved

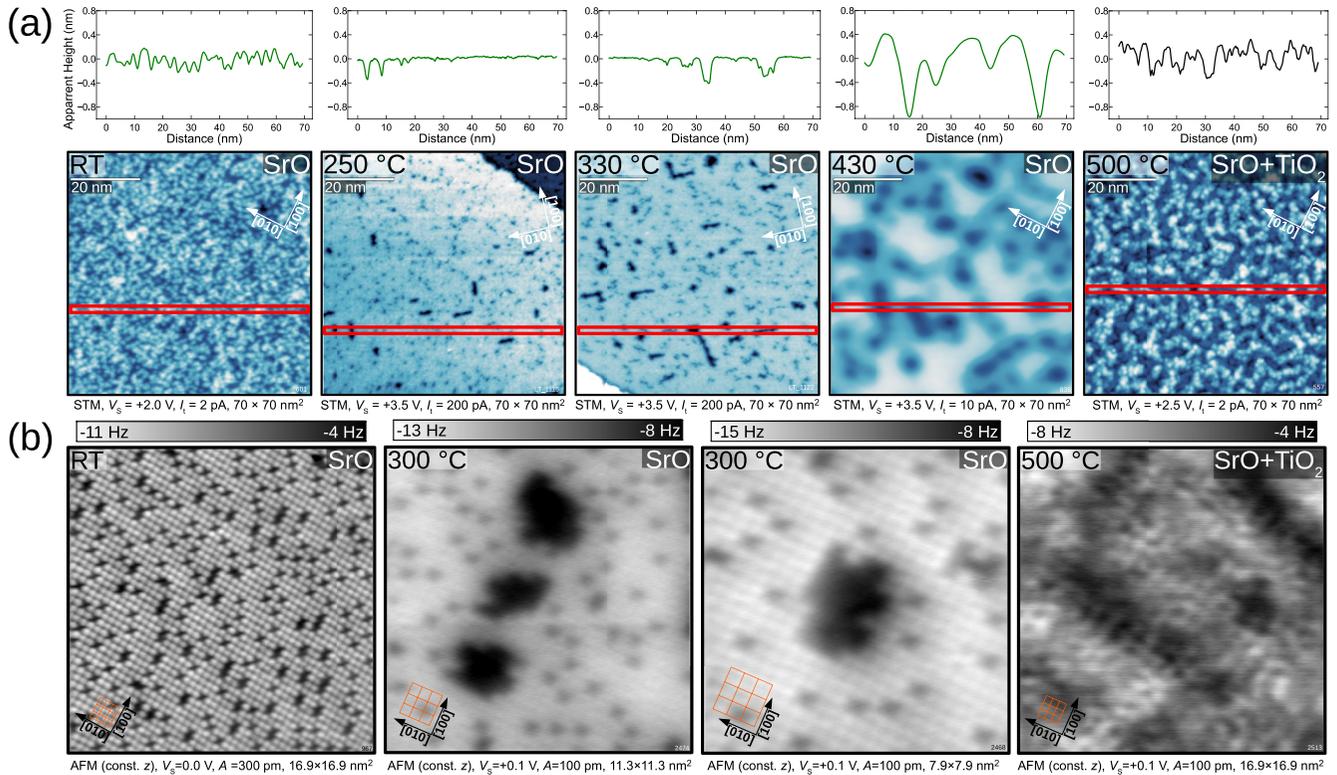


FIG. 2. SrO termination of the bulk-terminated SrTiO<sub>3</sub>(001) surface, as-cleaved and annealed at different temperatures. Sequence of (a) empty-state STM images with line scans extracted from the marked red rectangles; (b) atomically resolved constant-height AFM images, with the (1 × 1) grid shown in orange.

surface, consistent with a reduced band bending. Such surfaces also show a LEED pattern [Fig. 1(b)] with the lowest background intensity.

Further annealing results in the lateral growth of the pits, preferentially along the [100] and [010] directions. The STM images in Fig. 2(a) appear considerably rougher (up to 3 layers). Annealing the SrO termination at 500 °C results in a loss of the (1 × 1) ordering in AFM. Instead, images locally show a short-range (2 × 2) periodicity, while LEED retains the (1 × 1) symmetry. The surface corrugation deduced from the AFM images is less than half the unit cell height. STM images exhibit larger apparent height differences, but this can be partially attributed to electronic effects, when domains with different electronic properties form. At this stage of annealing, it is no longer possible to distinguish the previously SrO- and TiO<sub>2</sub>-terminated areas: the entire cleaved SrTiO<sub>3</sub>(001) surface shows the same morphology in STM and AFM images as in the rightmost panels of Figs. 2(a) and 2(b). The (1 × 1) LEED pattern of this surface is attributed to diffraction from the sub-surface layers, while the disordered surface layer contributes to the increased background intensity.

The evolution of the TiO<sub>2</sub> termination with temperature is shown in Fig. 3. After cleaving, the TiO<sub>2</sub> termination hosts Sr<sub>ad</sub><sup>2+</sup> adatoms [bright dots in Fig. 3(b)], complementary to the V<sub>Sr</sub><sup>2-</sup> vacancies at the SrO termination. In STM, the two terminations appear very similar. Annealing above 250 °C results in the formation of small, disconnected islands. The clustering of Sr<sub>ad</sub><sup>2+</sup> adatoms requires the presence of O<sup>2-</sup> to

compensate their electric charge, and indeed AFM images show the presence of anions [dark dots in Fig. 3(b)]. These SrO islands show tiny areas with a c(2 × 2) SrO structure on top of the TiO<sub>2</sub> termination. The intrinsic excess of Sr adatoms at the as-cleaved TiO<sub>2</sub> termination constitute an ideal seed for the crystal growth of the next perovskite SrTiO<sub>3</sub> layer, provided the temperature is sufficiently high for the diffusion of the adatoms and of oxygen to complete the SrO stoichiometry.

The c(2 × 2)-like areas spread with increasing temperature up to 430 °C. Islands grow more connected, while still not covering the entire surface. The maximum coverage of this SrO superstructure over the TiO<sub>2</sub> termination is limited by the initial 0.14 ML coverage of the Sr adatoms. When arranged in a c(2 × 2) superstructure, it can cover 28% of the surface area, close to the maximum coverage observed in AFM. After annealing at 500 °C the previous TiO<sub>2</sub> termination appears disordered and becomes indistinguishable from what was the SrO termination [rightmost panel of Fig. 2(a)]. Further annealing of the mixed-termination morphology at 600 °C [rightmost panel of Fig. 3(a)] does not improve the surface roughness, but instead increases the width of the pits and islands.

The two opposite terminations of the as-cleaved SrTiO<sub>3</sub>(001)-(1 × 1) surface experience a complementary evolution with annealing. The pit/island creation mechanism is induced by the presence of the intrinsic, polarity-compensating point defects, i.e., Sr vacancies and Sr adatoms [31]. Migration of these charged point defects

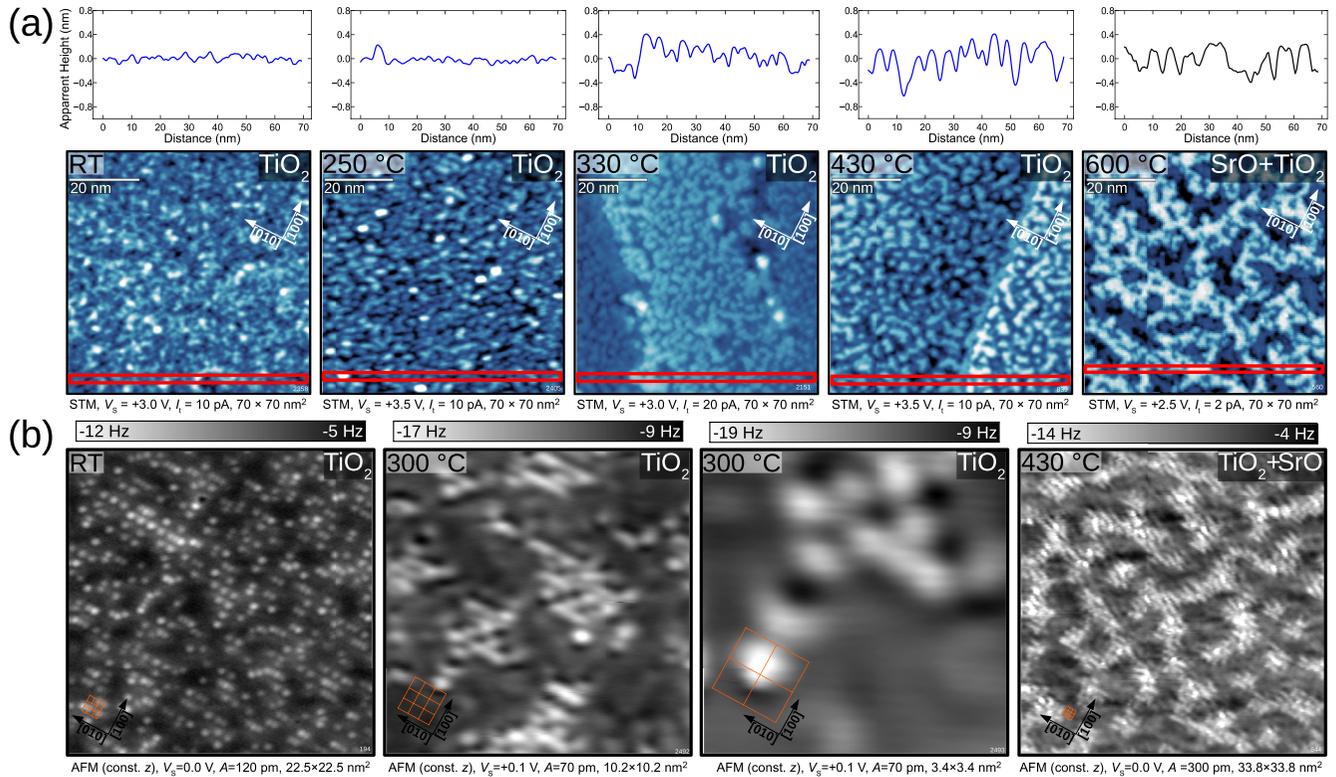


FIG. 3.  $\text{TiO}_2$  termination of the bulk-terminated  $\text{SrTiO}_3(001)$  surface, as-cleaved and annealed at different temperatures. Sequence of (a) empty-state STM images and line scans extracted from the marked red rectangle; (b) atomically resolved constant-height AFM images, with the  $(1 \times 1)$  grid shown in orange.

is activated at temperatures as low as 200 °C. Moreover, when the surface is additionally enriched by Sr adatoms *via* evaporation, the adatoms are mobile at both terminations and start to aggregate at temperatures as low as 150 °C, as shown in Ref. [44]. The disappearance/appearance of O likely originates from the exchange with the subsurface region, because lateral diffusion across the whole micrometer-wide domains is unlikely [45,46]. The temperature range for migration of vacancies is slightly lower than reported in the literature for  $\text{SrTiO}_3$  [47,48], but can be rationalized by the presence of electric fields related to the charged defects.

Since the intrinsic point defects dominate the thermal behavior of the cleaved crystals, annealing excursions were also conducted on  $\text{SrTiO}_3$  samples prepared by a wet chemical treatment that exposes only the  $\text{TiO}_2$  termination; full details are laid out in the SM [44]. Two cut-and-polished  $\text{SrTiO}_3(001)$  crystals, again with 0.7 at.% Nb doping, were cleaned *ex situ* and boiled in ultrapure water to etch away the soluble SrO termination [22]. One sample was baked in air at 950 °C prior to introduction to UHV (to create large, flat terraces) and turned out to be contaminated with carbon, alkali, and alkaline earth metals, see Ref. [44]. The second sample was introduced to UHV directly after wet cleaning and was contaminated with carbon only.

Figure 4 shows the temperature evolution of the latter sample. After annealing to mild temperatures, LEED shows a distinct  $(1 \times 1)$  pattern, and large-area STM images show

flat terraces. In AFM, however, clumps are visible, likely due to contamination. A substantial C 1s signal in XPS [Fig. 4(d)], indicates that the contaminants are carbon-based organics. Annealing at 500 °C–650 °C in  $1 \times 10^{-7}$ – $1 \times 10^{-6}$  mbar  $\text{O}_2$  back-pressure for 1–2 h gradually removed the C, but constant-height AFM still shows a surface covered by undetermined hillocks, with no hints of the underlying substrate. A significant reduction of C occurred only after annealing at 700 °C in  $1 \times 10^{-7}$  mbar  $\text{O}_2$  for 2 h. This treatment resulted in a reconstructed surface with a  $(\sqrt{13} \times \sqrt{13})R33.7^\circ$  superstructure [49,50] clearly visible in LEED and the constant-height AFM image in Fig. 4(c).

Results presented here directly demonstrate that the LEED diffraction patterns (and especially less-sensitive RHEED patterns [51]) are not a reliable indicator of an unreconstructed  $\text{SrTiO}_3(001)$  surface. Since no previous work explicitly showed an atomically resolved  $(1 \times 1)$  surface, it is questionable whether a pristine, unreconstructed  $\text{SrTiO}_3(001)$  surface was ever encountered. A plethora of intriguing phenomena observed on this surface, such is the appearance of a two-dimensional electron gas [11,12,52–54], can therefore be assigned to occur in the subsurface layers and potentially be protected by a contaminated or a disordered surface layer. Moreover, theoretical considerations assign  $\text{SrTiO}_3$  solids to be either “weakly polar” [55,56] or completely nonpolar [57,58] along the [001] direction, which implies ready availability of pristine  $\text{SrTiO}_3(001)$  surfaces—this is the basis for

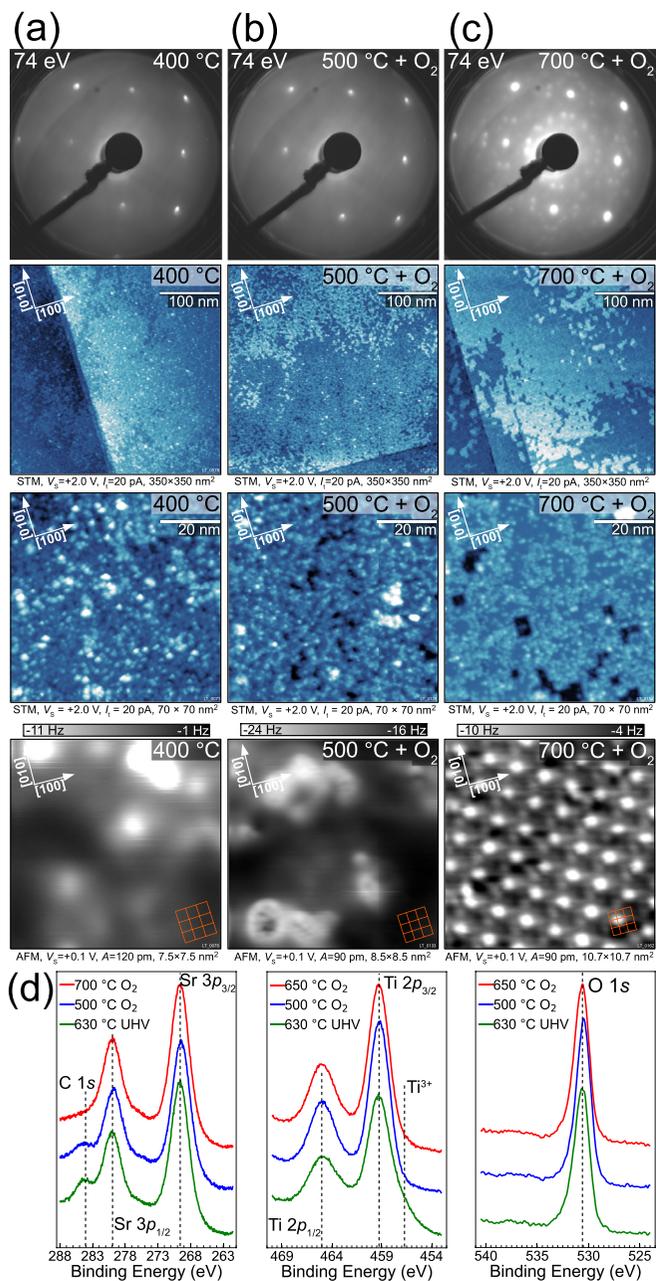


FIG. 4. Cut-and-polished TiO<sub>2</sub>-terminated SrTiO<sub>3</sub>(001) surface prepared by *ex-situ* wet-chemical treatment. (Top to bottom) LEED, large- and small-area empty-states STM, and AFM images after annealing at (a) 400 °C in UHV, (b) 500 °C, and (c) 700 °C in 1 × 10<sup>-6</sup> mbar O<sub>2</sub>. (d) XPS core-level spectra of the main elements at different annealing conditions, obtained with Al K $\alpha$  in grazing emission.

the common belief that it is easy to prepare pristine, unreconstructed SrTiO<sub>3</sub>(001) surfaces. Our work conclusively shows that the use of bulk-terminated surfaces in theoretical modeling does not reflect reality and may thus lead to imprecise predictions; this is additionally supported by a well-known proclivity of these surfaces for reconstructions [17,25,30,49,50]. Interestingly, our results indicate that the presence of excess material (possibly in the form of extrinsic contamination) at the top of the surface could be responsible for stabilizing the (1 × 1) termination. Such is the case of SrTiO<sub>3</sub>(001) surfaces used as substrates for heteroepitaxy, where the interface with high-quality thin-film structures is clearly crystalline and unreconstructed [59–63].

In summary, the search for an SrTiO<sub>3</sub>(001)-(1 × 1) surface that can be considered “pristine”—crystalline and well-ordered, with a negligible amount of defects and contaminants—was not successful so far. As-cleaved surfaces come closest, but necessarily contain both, SrO- and TiO<sub>2</sub>-terminated domains (albeit of considerable size), and charged point defects. The temperature-induced transformation to an ill-defined, disordered top layer indicates that the (1 × 1) has a high surface energy and is only metastable. The techniques generally applied to judge surface quality (electron diffraction, XPS, large-area STM or ambient AFM) give results that would be consistent with a perfect (1 × 1) termination; but are contradicted by atomically resolved nc-AFM. The same is true for the etched TiO<sub>2</sub>-terminated surfaces that are used to great extent as substrates in the growth of heteroepitaxial oxide films. While such surfaces can display a flat morphology with a high-quality diffraction pattern, nc-AFM shows no signs of the unreconstructed surface. The temperature required for removing carbon lies above the stability region of the bulk-terminated surface.

The (001) surfaces of SrTiO<sub>3</sub> and other perovskites continue to be of great interest for both, probing their intrinsic properties and as substrates for heteroepitaxy. As the results presented here show, the assumption of an atomically clean, crystalline bulk-termination might not be warranted. This should be considered in the proper interpretation of experimental data.

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