

Title:

Single-Layer TiO_x Reconstructions on SrTiO₃ (111): ($\sqrt{7} \times \sqrt{7}$)R19.1°, ($\sqrt{13} \times \sqrt{13}$)R13.9°, and Related Structures

Authors:

Tassie K. Andersen ^{a,*}, Shuqiu Wang ^b, Martin R. Castell ^b, Dillon D. Fong ^c, and Laurence D. Marks ^a

^a Department of Materials Science and Engineering, Northwestern University, Evanston, Illinois 60208, United States

^b Department of Materials, University of Oxford, Parks Road, Oxford OX1 3PH, UK

^c Materials Science Division, Argonne National Laboratory, Argonne, Illinois 60439, United States

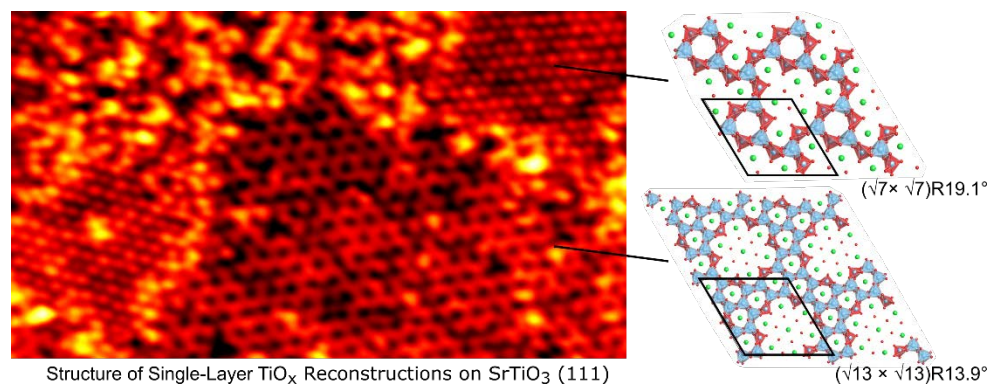
Corresponding author: TassieAndersen2013@u.northwestern.edu

Abstract:

The atomic structures of two reconstructions, ($\sqrt{7} \times \sqrt{7}$)R19.1° and ($\sqrt{13} \times \sqrt{13}$)R13.9°, on the SrTiO₃ (111) surface were determined using a combination of density functional theory and scanning tunneling microscopy data and APW+lo density functional theory minimizations and simulations. These reconstructions belong to the same structural family made up of an interconnected, single layer of edge-sharing TiO₆ and TiO₅ octahedra. This family of reconstructions between 0.5 and 1.5 excess TiO₂, representing the lowest-reported TiO₂ coverages for reconstructions on this surface. This family is found to include the previously-solved (2×2)a reconstruction. They all follow a simple rule for surface composition, which serves as a tool for better understanding and predicting the structure of other

reconstructions of arbitrary surface unit cell size on SrTiO₃ (111). This reconstruction family and the calculations of surface energies for different hypothesis structures also shed light on the structure of Schottky defects observed on these reconstructed SrTiO₃ (111) surfaces.

Graphical Abstract:



Keywords: DFT; Polar oxide surfaces; surface structure; oxide surfaces; surface defects; strontium titanate

1. Introduction

The surface of SrTiO₃ is of great interest for catalysis [1, 2], as a substrate for oxide thin film growth [3, 4], and for applications in oxide electronics [5-10]. As an archetypal perovskite material, SrTiO₃ represents a structural ideal; it is cubic and lacks both octahedral rotations and rhombohedral distortions at room temperature. However, its relative simplicity belies the complexity hinted at by the multitude of surface structures reported on this material.

Even for the most straightforward, commonly-utilized (100) termination of SrTiO₃, a large number of reconstructions have been reported [11-32], some of which remain unsolved. Many of the solved structures have a TiO₂ double layer with units of octahedral TiO₆ and TiO₅[] (where [] is an oxygen vacancy site) [29, 30, 33-35]. The field is no less crowded for the (110) termination of SrTiO₃ [36-41], where reconstructions including the (*n* × 1) series [40, 41] are made up of rings of tetrahedral TiO₄ units while the (2 × *n*) nanostructures [42] are made up of TiO₅[] and TiO₆ units in an interconnected matrix yielding differently sized, surface unit cells lacking overall formal charge.

By comparison, the SrTiO₃ (111) surface is both less exhaustively studied and more complex. Bulk SrTiO₃ (111) can be thought of as a stacking of alternating layers of (SrO₃)⁴⁻ and (Ti)⁴⁺. Reconstructions reported on this surface have been observed to depend heavily on substrate preparation conditions and include a (1 × 1) [43-45], (9/5 × 9/5) [11, 46, 47], two (2 × 2) [48], a (√7 × √7)R19.1° [49], (3 × 3) [11, 46, 47], (√13 × √13)R13.9° [49], (4 × 4) [11, 46, 47], (5 × 5) [47], and (6 × 6) [11, 46, 47]. Of these, only the structures of the two (2 × 2), the (3 × 3), and (4 × 4) have been determined [48]. These reconstructions were found to have structures made up of elements from both the (100) and (110) surfaces. All are terminated with double TiO_x layers. The underlying layer is composed of octahedral TiO₆ and TiO₅[], like the (100) surface, while the TiO_x layer closest to vacuum is formed by interconnected TiO₄ tetrahedra, like the (110) surfaces.

Here, we solve the structures of the (√7 × √7)R19.1° (RT7) and (√13 × √13)R13.9° (RT13) reconstructions on SrTiO₃ (111) using a combination of scanning tunneling microscopy (STM) and density functional theory (DFT) modeling. These structures are composed of octahedral TiO₆ and TiO₅[] units like those found on the (100) surface, consistent with elements of already-identified SrTiO₃ (111) reconstructions. When considered together, these structures belong to a family of SrTiO₃ (111) reconstructions that can be generated by examining tilings of TiO₅[] and TiO₆ of increasing size.

2. Experimental

Single crystals of 0.5 wt% Nb-doped SrTiO₃ (111) with epi-polished surfaces were supplied by PI-KEM, U.K. Surface preparation was performed in a JEOL JSTM4500xt ultrahigh vacuum (UHV) chamber. Samples were introduced without any pre-treatment into the chambers and annealed in UHV (chamber base pressure of 10⁻⁸ Pa) at 850 °C for 30 min. STM images at constant current were taken at room temperature using an etched tungsten tip. A detailed description of the sample preparation and STM imaging conditions can be found in reference [49].

All DFT calculations were performed using an all-electron augmented plane wave + local orbital WIEN2k code [50]. The PBEsol [51] generalized gradient approximation and the revTPSS method [52] were employed, with an on-site exact exchange fraction of 0.5 for the Ti-d orbital electrons, similar to previous work [35]. Atomic muffin-tin radii were set to 1.55, 1.71, and 2.21 Bohrs for O, Ti and Sr respectively, with an r*kmax of 6.20. For all calculations a Brillouin-zone reciprocal space sampling equivalent to a 4 × 4 in-plane mesh for a (111) 1 × 1 cell. Lattice parameters for the in-plane directions of the surface unit cell were set to those of the relevant DFT optimized bulk unit cell. To avoid errors a 1 × 1 × 10 supercell with at least 1.6 nm of vacuum was employed when constructing slab calculations. Atomic positions and electron density were converged simultaneously using a quasi-Newton algorithm [53] with surface cell convergence better than 0.01 eV/1 × 1. Surface energy per (1 × 1) surface unit cell was calculated as $E_{surf} = (E_{slab} - E_{STO}N_{STO} - E_{TiO_2}N_{TiO_2})/(2 * N_{1 \times 1})$, where E_{slab} is the total enthalpy of the slab, E_{STO} for a single bulk SrTiO₃ unit cell, N_{STO} the number of bulk SrTiO₃ unit cells present, E_{TiO_2} the total enthalpy of bulk rutile TiO₂, N_{TiO_2} the number of excess TiO₂ units, and $N_{1 \times 1}$ the number of surface (1 × 1) unit cells. Both N_{STO} and N_{TiO_2} are determined by finding the total number of atoms in the slab construction (complete with reconstructed surface) used and determining

the values of n and m for $n\text{SrTiO}_3 \cdot m\text{TiO}_2$. When surface energy is plotted against TiO_2 -excess, as in the convex hull construction, this quantity is found by normalizing to surface area such that $\text{TiO}_{2\text{excess}} = (N_{\text{TiO}_2}) / (2 * N_{1 \times 1})$. This method resulted in an error of approximately 0.05 eV/ 1×1 surface cell.

Low energy structures from DFT were checked using STM simulations based on a modified Tersoff-Hamann approximation [54]. Additional details regarding this simulation method can be found in reference [55] and in the Supplemental Material (SUPPL. FIG. 1).

3. Results

An iterative method was used to find solutions for the RT7 and RT13 structures. Experimental STM, from which unit cell size, symmetry, and prominent electron density features were obtained, informed the development of structure hypotheses. Candidate structures were relaxed and their surface energies calculated using DFT. Structures were refined if necessary by comparison of the simulated STM images with the experimental data.

Imaging of the samples by STM with RT7 and RT13 reconstructions shows terraces and jagged step edges that do not follow a preferential crystallographic direction. Much of the surface is covered by ordered RT7 or RT13 domains, although significant disorder is present between the domains. Figure 1 shows an STM image of a typical sample where both RT7 and RT13 domains are present. Additional STM of these reconstructions on different samples are provided in the Supplemental Material (SUPPL. FIG. 2). Two rotational domains are observed when comparing the two RT7 areas; this feature is also present in other samples for the RT13 [49]. The unit cells of the two reconstructions as well as their rotational domains are shown with respect to the bulk SrTiO_3 (111) surface in Figure 2. In Figure 2 the rotational domains of the RT7 reconstruction are indicated by Greek letters α and β . The STM image of the RT7 structure resembles a hexagonal-close packed arrangement of bright spots on a dark background, while

the RT13 structure shows the opposite contrast and is better described as a bright honeycomb-like structure. Unit cell averaging is performed over repeated defect free unit cells of the RT7 and RT13 reconstruction using the process described by Jones et. al.[56]. The p3 symmetry of both reconstructions can then be identified in Figure 1 (b, c) where the unit cells are highlighted by the white, dashed outlines.

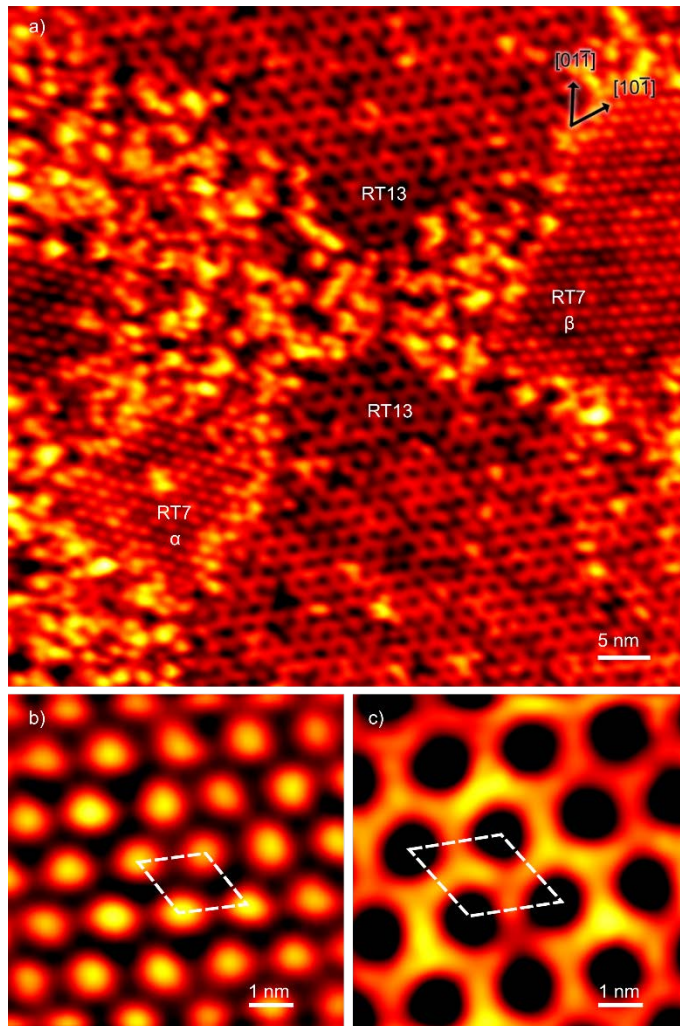


FIG. 1. (a) STM image (+2.9 V sample bias, 0.3 nA tunneling current) showing RT7 and RT13 domains. Greek letters α and β indicate the two rotational domains of RT7. (b) Unit cell averaged STM images of the RT7 reconstruction (+2.1 V bias, 0.1 nA current) and (c) the RT13 reconstruction (+3.6 V bias, 0.1 nA current), dashed parallelograms outline unit cells of reconstructions.

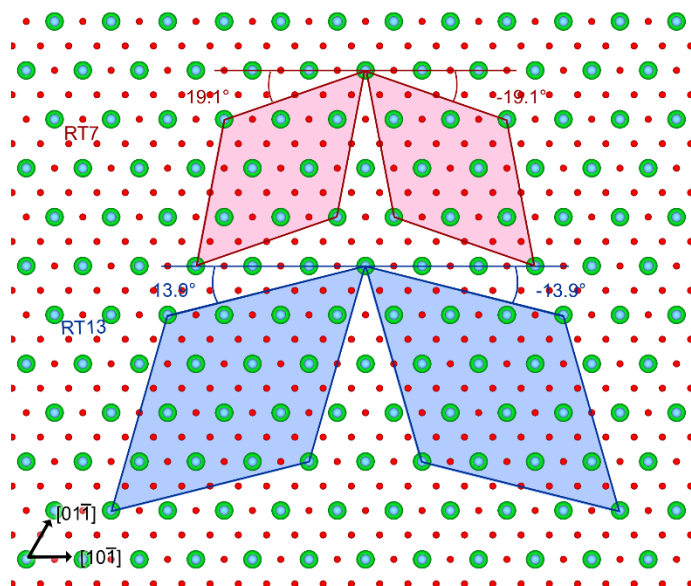


FIG. 2. Unit cells of two rotational domains of RT7 (pink) and RT13 (blue) compared to the underlying in-plane bulk unit cell. Atoms of Sr (green), Ti (blue), and O (red) are shown.

Surface structures for SrTiO₃ (111) must have no overall formal charge, must be stoichiometric (i.e. with no partial occupancy of sites), and additionally are TiO₂-rich based on experimental data [49]. This leads to all of the reconstructions discussed having an overall formula described by $n\text{SrTiO}_3 \cdot m\text{TiO}_2$ where n and m are integer values. These constraints, paired with the observations from STM, lead to a limited number of possible structures following rules to be discussed in subsequent sections. Surface energies calculated from DFT for RT7 and RT13 solutions are plotted in Figure 3. Energies from theoretical structures representing low and high TiO₂-excess, chosen since they were found to be the lowest-energy possibilities among many hypothetical structures [48], are also plotted, forming endpoints. The endmember structure referred to as “Low” in Figure 3 is composed of a single-layer, zig-zagging linear arrangement of TiO₅ units (this can be seen as a linear arrangement of TiO₅ and TiO₄ units as described in ref [48] if only short Ti-O bonds between 1.8 and 2.3 Å are considered). A high-coverage structure, referred to as “High” in Figure 3, is made up of a two-layer structure. The first layer consists of

TiO_6 units at atomic sites which are an extension of the bulk layers below, the second layer is made of interconnected rings of TiO_5 units (this outer layer can be seen as TiO_5 and TiO_4 units as described in ref [48] if only short Ti-O bonds between 1.8 and 2.3 Å are considered). Together with the experimentally solved $(2 \times 2)_a$ reconstruction, they form a convex hull construction. In this work these two structures will be referred to as “High” and “Low”, with the third structure plotted in the convex hull in Figure 3 referred to as “ $2 \times 2a$ ”. Please note that in ref [48] these are referred to by the terms “High”, and “Small” (ref [48] supplement), “Low”, “L4” (ref [48] supplement), and “ $2 \times 2a$ ”, “O2x2” (ref [48] supplement). If the calculated surface energy for a given structure is within error of an interpolated line between these convex hull points it is considered a stable structural possibility. In Figure 3, the lowest-energy solutions that best match the experimental STM data are those marked RT7b and RT13b. The other solutions plotted, RT7a and RT13a, are additional low-energy structure solutions. Given the accuracy of the DFT functionals, the convex hull and proposed solutions are consistent with experiment as described in previous work [48]. Both solutions for the RT7 and RT13 are lower in excess TiO_2 than the previously reported $(2 \times 2)_a$, making them the lowest excess TiO_2 reconstructions solved on the SrTiO_3 (111) surface. The TiO_2 excess for both structures, 1.071 for RT7b and 1.038 for RT13b, is similar and consistent with the STM results showing both domains on a given sample. This reinforces the observation that identical preparation methods lead to similar surface compositions.

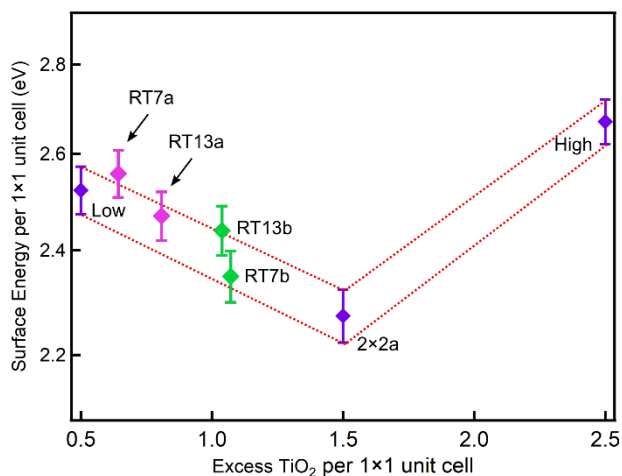


FIG. 3. Surface energies in eV/(1 × 1) surface unit cell plotted versus excess TiO₂ per (1 × 1). Results are from the revTPSS calculation, and the dotted lines show results from the convex hull construction.

The simulated STM image of the RT7b structure, shown in Figure 4 (a, b), is the closest match among the low-energy RT7 candidate structures to experimental data. These structures (RT7b and RT13b) are shown in an enlarged view and from an in-plane axis in the Supplemental Material (SUPPL. FIG. 3). The bright dot features are reproduced at spacings that match experiment, and the three-fold rotation symmetry is prominent. The other low-energy structure, RT7a, is shown for comparison in Figure 4 (c, d). The RT13 structure most consistent with experiment, RT13b, is also shown in Figure 4 (e, f), and the features of its simulated STM image recreate the bright honeycomb-like pattern faithfully, while the other low-energy structure, RT13a, is shown in Figure 4 (g, h). In these reconstructions, the dark areas of the experimental STM image correspond to areas lacking TiO_x coverage or areas where TiO_x units are present in low density such that they are not connected to as many neighboring TiO_x units, as the structures in Figure 4 (b, d, f, and h) illustrate.

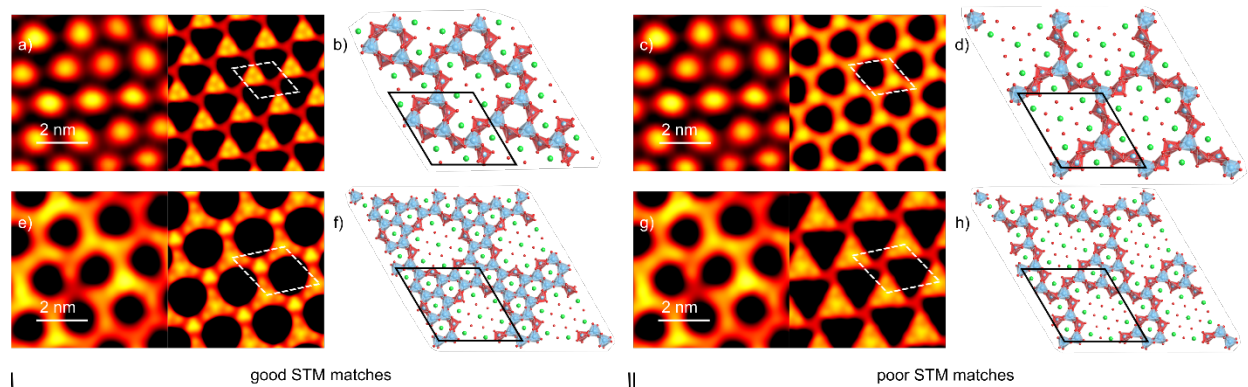


FIG. 4. (a) Unit cell averaged STM image (+2.1 V sample bias, 0.1 nA tunneling current) of RT7 with simulated RT7b overlaid in the middle and (b) structure diagram with TiO₅ octahedra in red, TiO₆ octahedra in blue, and Sr atoms in green. (c, d) Show the same information for RT7a respectively. (e)

Unit cell averaged STM (+3.6 V bias, 0.1 nA current) of RT13, simulation RT13b overlaid to the right and (f) diagram of structure. (g, h) Show the same information for RT13a respectively.

Both the RT7b and RT13b structures are made up of an interconnected network of two structural features. A single surface layer of octahedrally coordinated TiO_6 and TiO_5 units forms the basis of both reconstructions. Each TiO_6 unit shares three polyhedron edges with TiO_x units in the same surface plane, while TiO_5 units share only two edges. The Ti-O bond lengths in the surface TiO_6 and TiO_5 are both comparable to those in the bulk. Surface Ti to subsurface O bonds are slightly longer than in the bulk (2.209 Å for TiO_6 and 1.994 Å for TiO_5 vs 1.968 Å in the bulk), which is unsurprising as the surface TiO_x units are packed more closely than in the bulk, favoring outward expansion. Bond-valence sums indicate that the titanium and oxygen atoms are close to the 4+ and 2- nominal valences, respectively, as expected from a stable structure [57]. Structures refined from DFT are provided as crystallographic information files (CIF) in the Supplemental Material accompanied by a key indicating which file names correspond to which structures.

4. Discussion

Analysis of these reconstructions reveals a common model for their generation, one that was in fact used to identify initial structural hypotheses. The two reconstructions treated in this work share common structural units. They consist of a single TiO_x terminating layer built up on the bulk-like SrO_3^{4-} (111) atomic plane. This TiO_x layer is an interconnected network of octahedral TiO_5 and TiO_6 units. Overall lack of formal charge is maintained and each oxygen atom in the layer closest to vacuum is bonded to two cations. In the case of the RT7b reconstruction, avoiding formal charge is done by removal of a single strontium atom per surface reconstruction unit cell from the otherwise bulk-like SrO_3^{4-} layer. This description is codified in Figure 5, where the imposed triangular grid has intersections

at the position of Sr atoms in the outermost bulk-like SrO_3^{4-} layer. The spaces within the grid represent available sites for placement of TiO_5 and TiO_6 units (red and blue respectively).

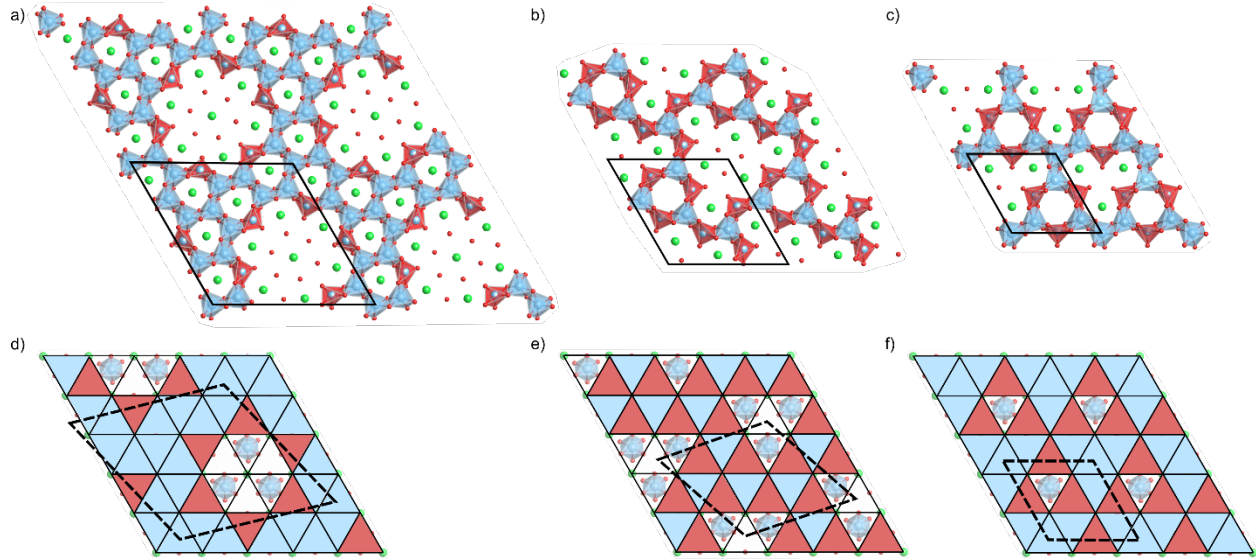


FIG. 5. (a) Diagram of RT13b, (b) RT7b, and (c) $(2 \times 2)a$ where TiO_5 octahedra are red, TiO_6 octahedra blue, and Sr atoms are green. (d) Grid imposed on bulk SrTiO_3 (111) to codify RT13b, (e) RT7b, and (f) $(2 \times 2)a$.

One structure, a theoretical low-energy SrTiO_3 (111) surface not plotted in Figure 3 but reported as “Model 8” in ref [58], and “Other” in ref [48] (referred to as “Other” herein) serves as a starting point for generation of the RT7b, RT13b, and other reconstructions of this single Ti-layer family. It is made up of a bulk-like SrO_3^{4-} layer with every atomic site (other than those above the strontium atoms) occupied by a titanium atom such that the terminating surface is an unbroken matrix of TiO_6 units. If this were to be illustrated using the coded method described above, it would appear as an unbroken field of blue triangles occupying every grid space. This structure meets the criterion of being free of overall charge and can be represented by the formula $n\text{SrTiO}_3 \cdot m\text{TiO}_2$.

If atoms are removed from this surface, creating surface vacancies, according to integer amounts of either SrTiO₃ or TiO₂, no partially occupied sites exist, there is no overall formal charge for the structure, and a variety of permutations representing possible structures can be generated. Alternatively, experimental data can be used to inform where these vacancies, especially those of the topmost TiO_x layers, are most likely to be, as was the case for structures presented here. In cases where the removal of one or more Sr atoms is necessary, the lowest-energy sites for removal, found through DFT simulation, are those with the highest number of neighboring TiO₅ and TiO₆ surface units. This is likely due to the fact that removing a Sr atom from these sites does little to impact the bonding environment of the nearby oxygen atoms.

Although both the RT7b and RT13b are rotated with respect to the bulk, this vacancy model extends to unit cells without these rotations. For example, the previously solved p3 (2 × 2)a structure [48] fits this model and is in fact the smallest possible unit cell for this family. It represents the case of the highest possible SrTiO₃ vacancy density where the p3 symmetry is maintained. A representation of the p3 (2 × 2)a, RT7b, and RT13b structures in the framework described above is illustrated in Figure 5. For the sake of clarity, any removed Sr atoms are not shown in the symbolic representations of Figure 5 (e, f). This representation makes clear which sites TiO₅ or TiO₆ units occupy. These representations also make the TiO₅:TiO₆ ratio easier to gauge at a glance and show how changing the number and placement of vacancies affects this ratio.

This model also provides a framework for understanding defects in reconstructions, particularly those observed in the STM images of the RT13 surfaces shown in Figure 6 (a). These defects appear as breaks in the honeycomb structure of the RT13, leading to the joining of two or more dark areas. If the RT13b structure is examined, some number, *n*, of TiO₂ units (or SrTiO₃ units) can be removed, as illustrated in Figure 6 (b, c). In Figure (b, c) the unit removed is circled in the upper left with the resulting structure after removal shown in the center. While the examples shown maintain p3 symmetry, this is not a

necessary condition, and any combination of units can be removed to best capture the experimental STM intensities of a given defect. The Schottky defects illustrated in Figure 6 (b, c) represent possible structure solutions for defects such as the ones shown in Figure 6 a).

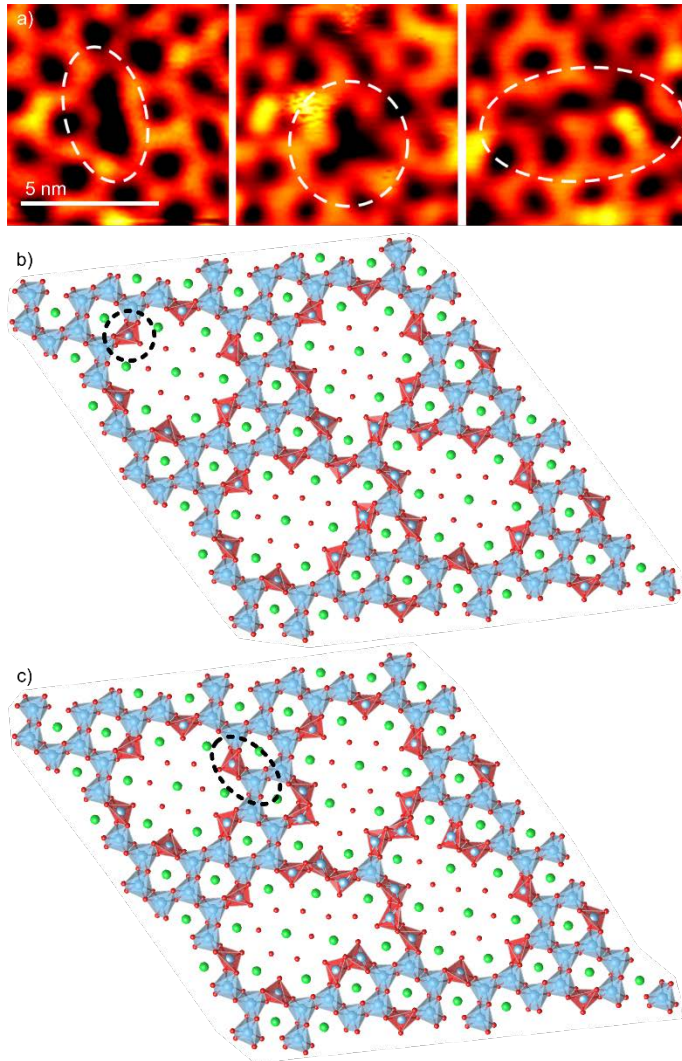


FIG. 6. (a) STM image (+2.9 V sample bias, 0.3 nA tunneling current) of defects in RT13. (b, c) Diagrams of RT13b showing possible Schottky defects where TiO_5 octahedra are red, TiO_6 octahedra blue, and Sr atoms are green.

While this model does not encompass all solved structures on the SrTiO_3 (111) surface, it can be applied to any reconstruction bearing only $p3$ symmetry regardless of rotation or size with respect to the bulk

unit cell. The RT7b and RT13b, along with p3 (2 × 2)a, provide insight into the structure of lower TiO₂-excess reconstructions where only a single layer of TiO_x is present. Additionally, they fit in with the other solved Ti double-layer reconstructions on this surface, both structurally and conceptually. The units of this TiO_x layer are identical to those present in higher-coverage surfaces, like the (3 × 3) and (4 × 4), which also contain TiO₅ and TiO₆ units. However, these single-layer reconstructions require no additional tetrahedral TiO₄, instead relying on their denser coverage to lower surface energy and provide sufficient electron density for oxygen atoms.

5. Conclusions

In summary, the structures of the RT7 and RT13 on the SrTiO₃ (111) surface were identified. The method used considered STM data to produce structural hypotheses that were relaxed via DFT to find low-energy candidates which were compared back to experimental data via STM simulation. The model discussed herein for reconstructions on the SrTiO₃ (111) surface serves as a starting point for generating structural solutions even with sparse data sets, which can be paired with DFT calculations to identify low-energy candidates. Although the hexagonal nature of this surface presents additional complexity, all possible reconstructions belonging to the described vacancy family of a given unit cell size could be generated via a properly constrained algorithm. Understanding the fundamental units of reconstruction families such as this allows reduction of the computation resources required in identifying structures and provides an opportunity to unify descriptions of reconstructions on a given material surface.

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