

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

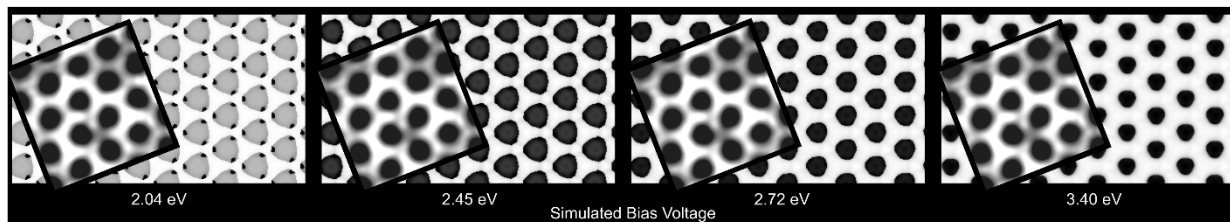
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Supplemental Material

Methods:

Additional Information on STM Simulations using DFT:

For STM simulations using the calculated electron density from DFT an energy window is populated around the Fermi energy, E_F , from E_{min} to E_{max} such that $E_{min} = E_F$ while $E_{max} = E_F + eV_b$ where V_b is the experimental bias voltage. Since these experiments are conducted at a high voltage the experimental voltage is used more as a benchmark and a variety of simulations are done, changing the size of the energy window around this value until the experimental STM is reproduced most closely. As an example the RT13b STM simulations are shown in SUPPL. FIG. 1.



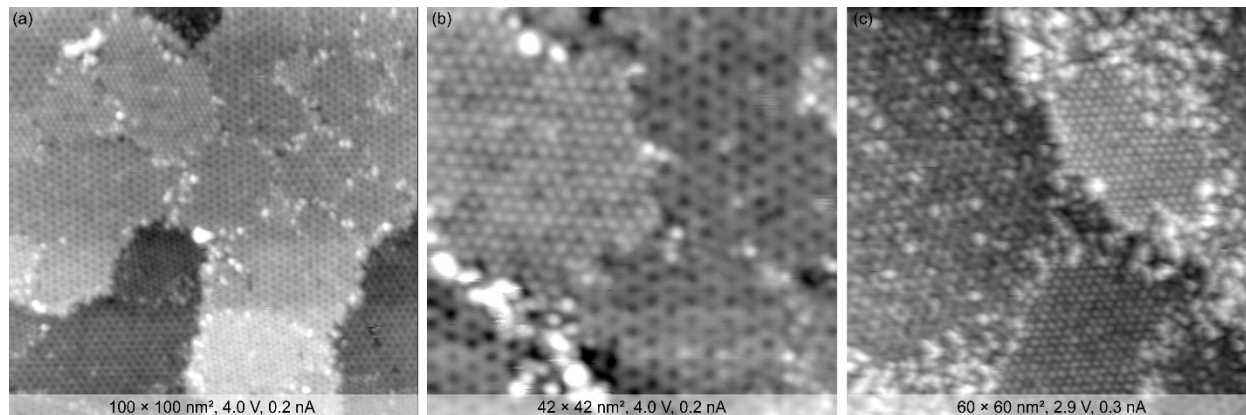
SUPPL. FIG. 1: Simulated STM of the RT13b reconstruction at different bias voltages indicated below the corresponding frame. The inset image in each frame is unit cell averaged STM (+3.5 V bias, 0.1 nA current) of the RT13 shown for comparison.

STM of the RT13b structure was simulated for bias voltage (eVb) values in the range of 2.04 eV to 3.40 eV. The reported bias voltage of the experiment was 3.5 V (or 3.5 eV). However, the simulation which best reproduces the experimental features is between 2.45 – 2.72 eV. Thus, the experimental value serves as more of a guide for determining what range of bias voltages should be simulated. The different simulated STM are all shown in the manuscript for the simulated bias that gives the closest match to the experimental. These simulation parameters are as follows: RT7a (1.90 eV), RT7b (1.90 eV), RT13a (2.72 eV), RT13b (2.72 eV).

Results:

Additional STM of RT7 and RT13 Reconstructions

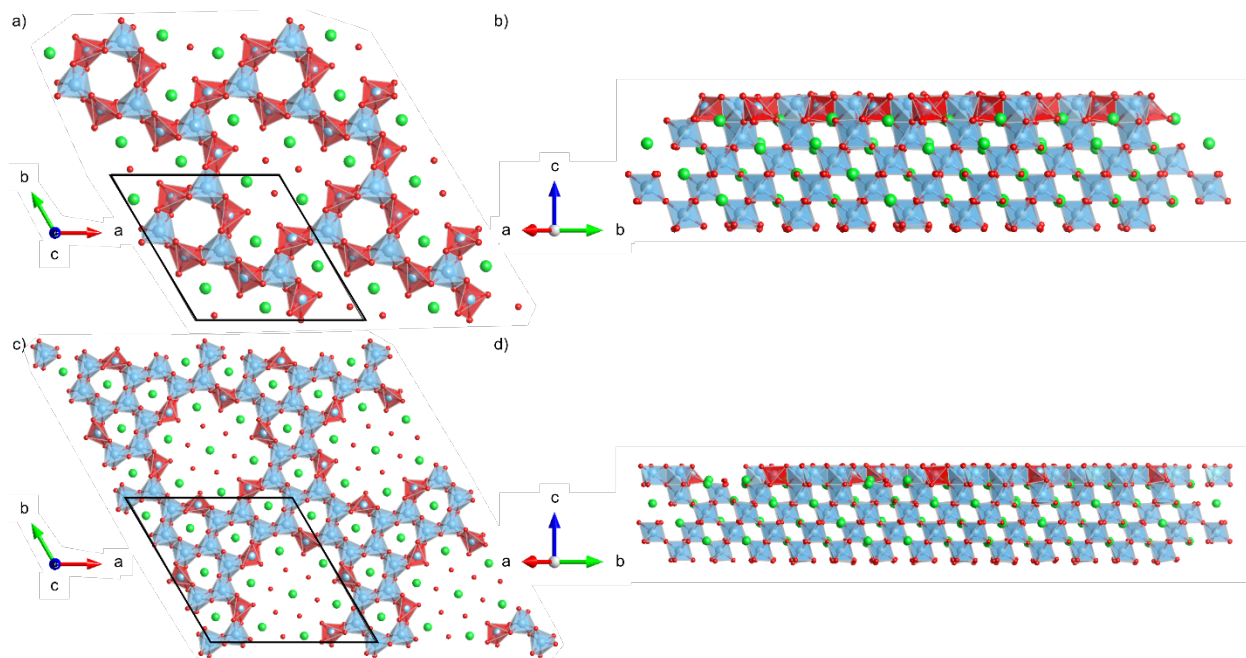
The RT7 and RT13 structures have been repeatedly generated with different STM imaging parameters, on different samples and observed in different STMs. Below, in SUPPL. FIG. 2, are additional images of the RT7 and RT13 on both different samples and different regions within a given sample. These images indicate that the occurrence of RT7 and RT13 regions on the same sample is not uncommon and that the reconstructions' production and observation is repeatable.



SUPPL. FIG. 2: STM images showing RT7 and RT13 domains: (a) & (b) from different samples as Figure 1, and (c) from the same sample as Figure 1 but different regions. The STM parameters are indicated on the images.

Structures of Lowest-Energy Solutions for RT7 and RT13 Reconstructions

A larger view of the low-energy structural solutions, RT7b and RT13b are shown in SUPPL. FIG. 3.



SUPPL. FIG. 3: Structure of the RT7b reconstruction viewed from above (a) and from the side (b) along an axis where the bulk structure of SrTiO_3 (111) is clear, showing the interconnected TiO_5 and TiO_6

octahedra in red and blue respectively and Sr atoms in green. (c, d) show the same information for the RT13b reconstruction.

List of Included cif (crystallographic information) Files and Descriptions:

SUPPL. TABLE 1: Surface enthalpies in units of $\text{eV}/1 \times 1$ for the structures reported using two different functionals. Please note the naming convention for these files is the same as the cifs included, the structure 'Other' is included as purely a structure reference and was not included in calculations.

Filename	Type	Excess TiO_2	revTPSS ($\text{eV}/1 \times 1$)	PBEsol ($\text{eV}/1 \times 1$)
Low	1×2	0.50	2.52	2.42
RT7a	$(\sqrt{7} \times \sqrt{7})\text{R}19.1^\circ$	0.64	2.56	2.54
RT13a	$(\sqrt{13} \times \sqrt{13})\text{R}13.9^\circ$	0.81	2.47	2.50
RT13b	$(\sqrt{13} \times \sqrt{13})\text{R}13.9^\circ$	1.04	2.44	2.50
RT7b	$(\sqrt{7} \times \sqrt{7})\text{R}19.1^\circ$	1.07	2.35	2.39
2x2a	2×2	1.50	2.27	2.33
Other	1×1	1.50	n/a	n/a
High	1×1	2.50	2.67	2.65