Supporting Information

Hydrogenated Anatase TiO_2 Single Crystals: Defects Formation and Structural Changes as Microscopic Origin of Co-Catalyst Free Photocatalytic H_2 Evolution Activity

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Experimental Section

PLD synthesis of 100 nm anatase layer on STO. The samples have been prepared by pulsed laser deposition (PLD), the experimental details are given elsewhere.[1]

Annealing. Epitaxial, undoped anatase thin films on STO substrate have been prepared using pulsed laser deposition (PLD). The crystallographic structure elucidation were described in detail elsewhere.[1] These anatase-STO SC were then exposed to a pure hydrogen annealing in a flow furnace at temperatures between 300 °C and 700 °C, and different duration from 1h to 16 h.

Photocatalytic H_2 evolution: Open-circuit photocatalytic H_2 evolution experiments were carried from anatase-STO single crystals immersed into an aqueous methanol solution (50 vol.%) in a quartz tube illuminated 24h with a 325 nm laser operating at 0.055 W (IK3552R-G, KIMMON). For the determination of the hydrogen evolution rates, the lasers was focused to a 1.8 mm spot size and the experiments were repeated at least three times. A gas chromatograph (GCMS-QO2010SE, SHIMADZU) with TCD detector was applied to determine H_2 concentration evolved from the different samples in the head space volume of the test tube. Reproducibility experiments were carried out from newly prepared samples treated under the same conditions.

Optical measurements: Diffusive reflectance spectra of the samples prepared at different temperatures were measured by a fiber-based UV-vis-IR spectrophotometer (Avantes, ULS2048) equipped with an integrating sphere AvaSphere-30 using AvaLight-DH-S-BAL balanced power light source. The optical bandgap of the samples was obtained by Kubelka-Munk equation using UV-vis diffuse reflectance spectra for the indirect allowed transitions (m = 0.5)[2].

X-ray analysis (XRD & XRR). All X-ray patterns were acquired by a Rigaku Smartlab 9 kW, equipped with a Johannson monochromator yielding a divergent copper $K_{\alpha 1}$ beam with a wavelength of 1.54 Å. For Bragg Brentano measurements the divergence (0.2°) of the beam was exploited and 2.5° soller collimators were used. An additional X-ray mirror (CBO-unit) was used to parallelize the beam in the vertical direction. In-plane 0.5° soller collimators were inserted for the GID and XRR measurements. For the GID experiments, the incident angle was 0.27°, thus below the critical angle for Anatase of 0.287°.

Atomic Force Microscopy AFM measurements were performed on a Park NX10 AFM from Parks Systems. NCHR Pointprobe cantilevers from NanoWorld were used. Each measurement was performed in non-contact mode with a set-point between 7 and 9 nm and a scan rate between 0.1-0.15 Hz. In each measurement a 50x50 μm surface was scanned. The measurements were performed on different, randomly chosen spots on each sample.

Focused ion beam preparation (FIB). The FIB lift-out was performed with a Helios NanoLab 660 dual beam system. In order to preserve the native crystal surface, a thick protective carbon protection layer was deposited before ion-beam processes milling. The final lamella were dependent on the sample and the position 50-120 nm thick. Ion-beam showering at 2keV beam energy was utilized as last step before the TEM investigations. In this way, the ion-beam induced sample damage was kept at minimum level.

Electron microscopy. transmission electron microscopy investigations were carried out on a ThermoFisher Scientific Titan Themis microscope operated at 300 kV. The microscope is equipped with monochromator, both probe-forming and imaging Cs correctors, a high efficiency Super-X EDX detector system and Gatan Quantum ERS system for electron energy loss spectroscopy. The STEM experiments were acquired using a probe-corrected probe with semi-convegence angle of 15.7 mrad. Typical probe current of 50-100 pA was applied for imaging, and 30-80 pA for EELS. For STEM imaging, high angle annual dark field (HAADF, angle range 65 – 300 mrad), annual dark field (ADF, angle range 18 – 60 mrad) annual bright field (ABF, angle range 8 – 17 mrad) and bright-field (BF, angle range 0-7.5 mrad) detectors were used to acquire simultaneously images of different contrast mode. During STEM-EELS data acquisition, great care was taken to mitigate the beam induced structural damage. We notice structural damage when apply an instantons dose above 50 pA * 1*1Å^2 *5ms = 1.56 *10^6 e$^-$/Å^2. EDXS data was acquired at a probe-corrected ThermoFisher Scientific Spectra 200 C-FEG. The cold field emission gun was operated at 200 kV. All data sets were acquired in [010] ZA, at a STEM magnification of 335 kx and a probe current around 60 pA. For EDXS quantification by Velox 3.0 a sample thickness of 100 nm, a material density of 3.9 g/cm^3 and Schreiber Wilms ionization cross-sections were utilized.

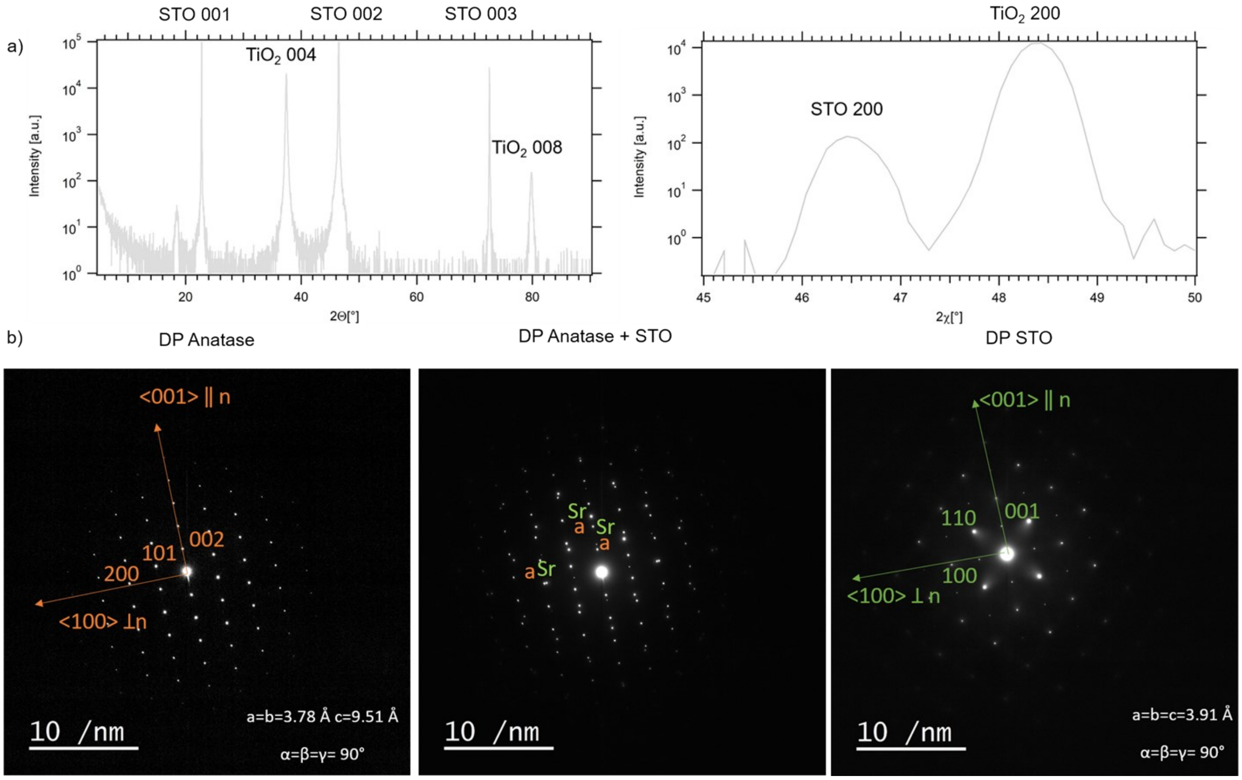

Figure SI1 a) XRD out-of (left) and in-plane (right) data of the reference sample. b) SAED patterns of the anatase film, the anatase STO interface and the SrTiO3 substrate. Both revealing the orientation relationship TiO2 (001)[100] || STO (001)[100].

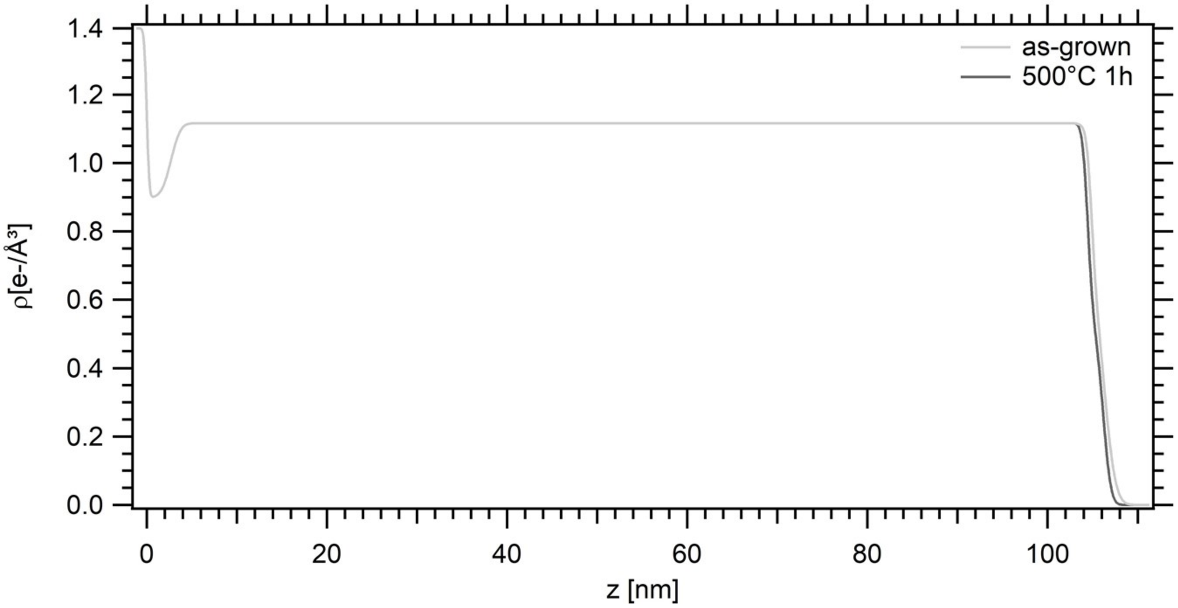

Figure SI2 Full range of the XRR electron density profile of the as-grown and 500°C 1h. Note the profiles only differ at the top of the film, an enlarged view of this part is shown in the main manuscript.

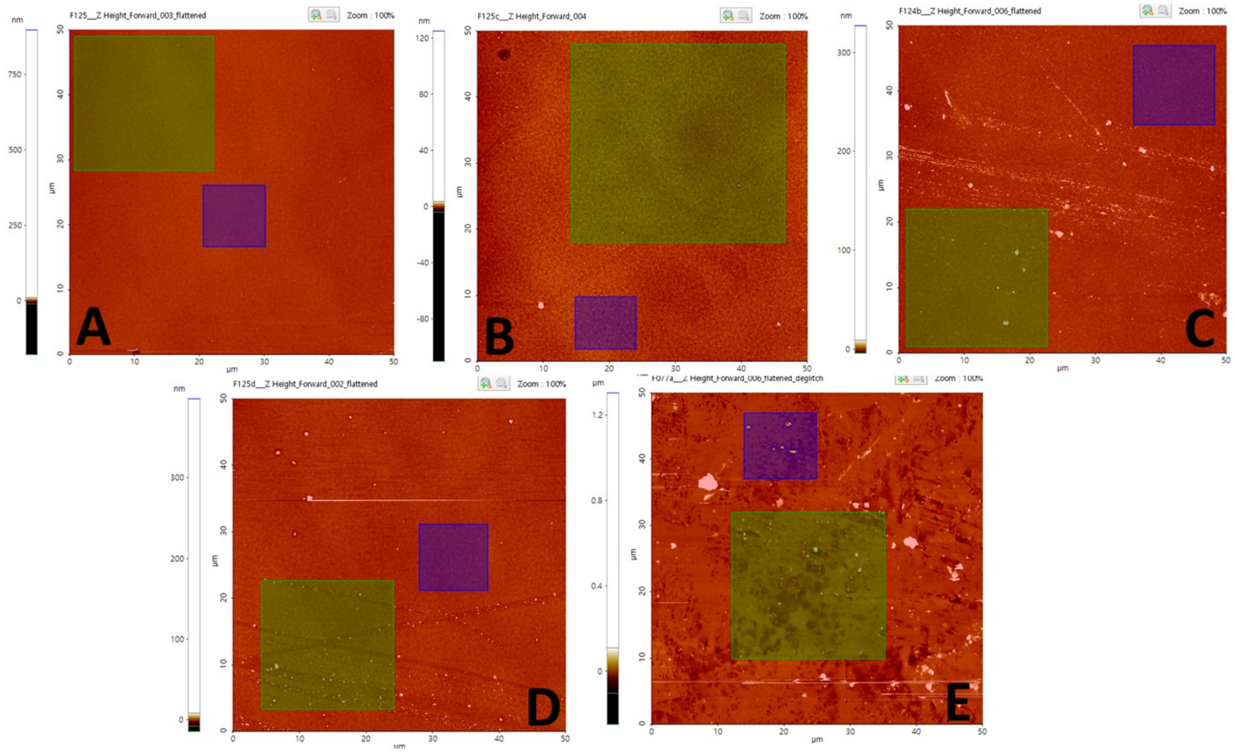

Figure. SI3 2D AFM images of different specimen. Images A-E correspond to as-grown, 500° 1h, 500° 9h, 500° 16h and 700° 1h respectively. The colored rectangles show different analyzed areas. Red is the whole image, green excludes extreme values and glitches whereas blue tried to cover a maximal undisturbed surface.

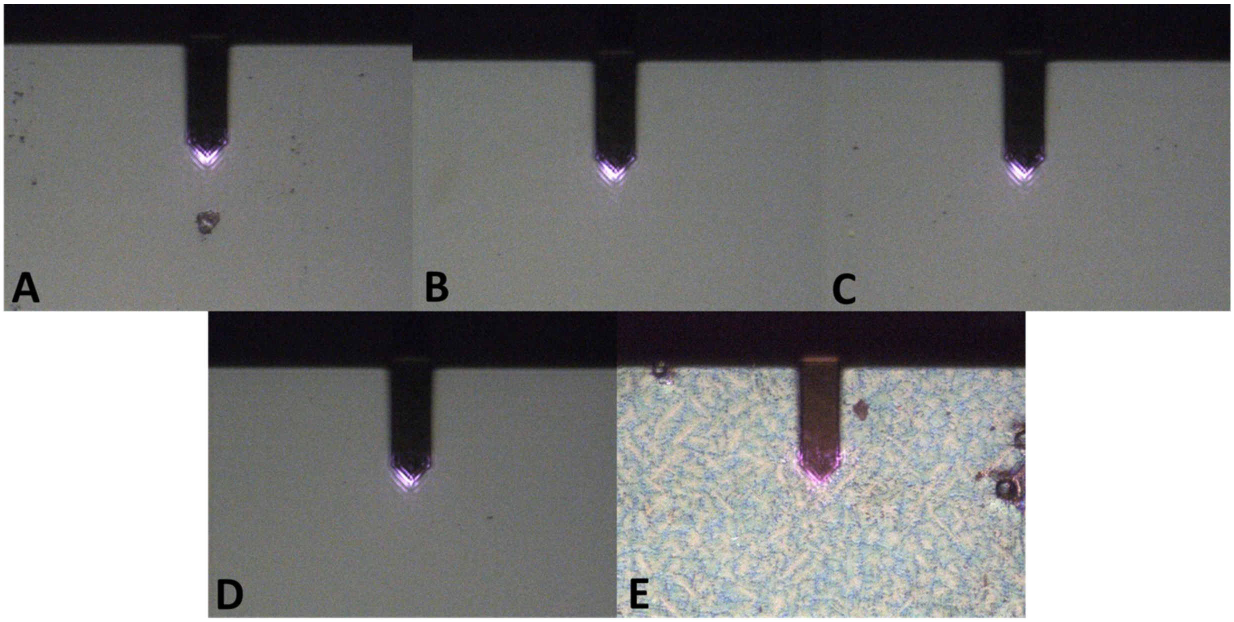

Figure. SI4 Microscopic images of the different specimen surfaces. Images A-E correspond to as-grown, 500° 1h, 500° 9h, 500° 16h and 700° 1h respectively.

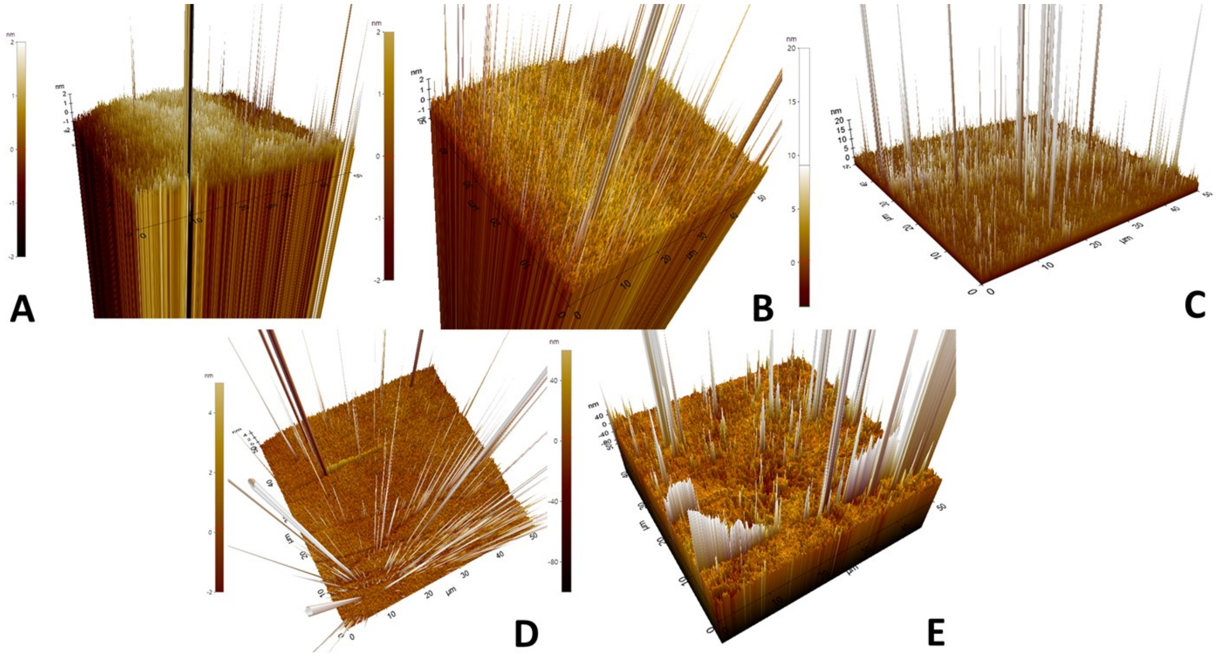

Figure. SI5 3-D projection of representative AFM Images of the different species. A-E correspond to as-grown, 500° 1h, 500° 9h, 500° 16h and 700° 1h respectively.

Specimen	R_q	R_{pv}
As-grown	**0.441 nm**	**14.857 nm**
500° 1h	**0.488 nm**	**11.18 nm**
500° 9h	**0.925 nm**	**44.55 nm**
500° 16h	**0.505 nm**	**15.63 nm**
700° 1h	**17 nm**	**236 nm**

Table SI1: Results of the AFM measurements for different specimens. R_q denotes the root-mean-square surface roughness, which is calculated from areas excluding height spikes and measurement anomalies (blue areas). R_{pv} denotes the difference between the highest peak and lowest valley in the measured area (red).

Specimen	c Axis [Å] (XRD)	a Axis [Å] (XRD)	c Axis [Å] (SAED, top)	c Axis [Å] (SAED, int.)	a Axis [Å] (SAED, top)	a Axis [Å] (SAED, int.)	d101 [Å] (SAED, top)	d101 [Å] (SAED, int)
As-grown	**9.608**	**3.758**	**9.55**	**9.57**	**3.74**	**3.76**	**3.50**	**3.50**
500°C 1h	**9.598**	**3.762**	**9.53**	**9.54**	**3.75**	**3.75**	**3.51**	**3.51**
500°C 6h	**9.583**	**3.764**	**9.55**	**9.56**	**3.76**	**3.76**	**3.51**	**3.51**
500°C 16h	**9.580**	**3.766**	**9.61**	**9.54**	**3.81**	**3.78**	**3.54**	**3.53**
700°C 1h	**9.560**	**3.777**	**9.56**	**9.50**	**3.78**	**3.77**	**3.54**	**3.52**

Table SI2 lattice parameters extracted from XRD in-plane, out-of-plane and SAED measurements

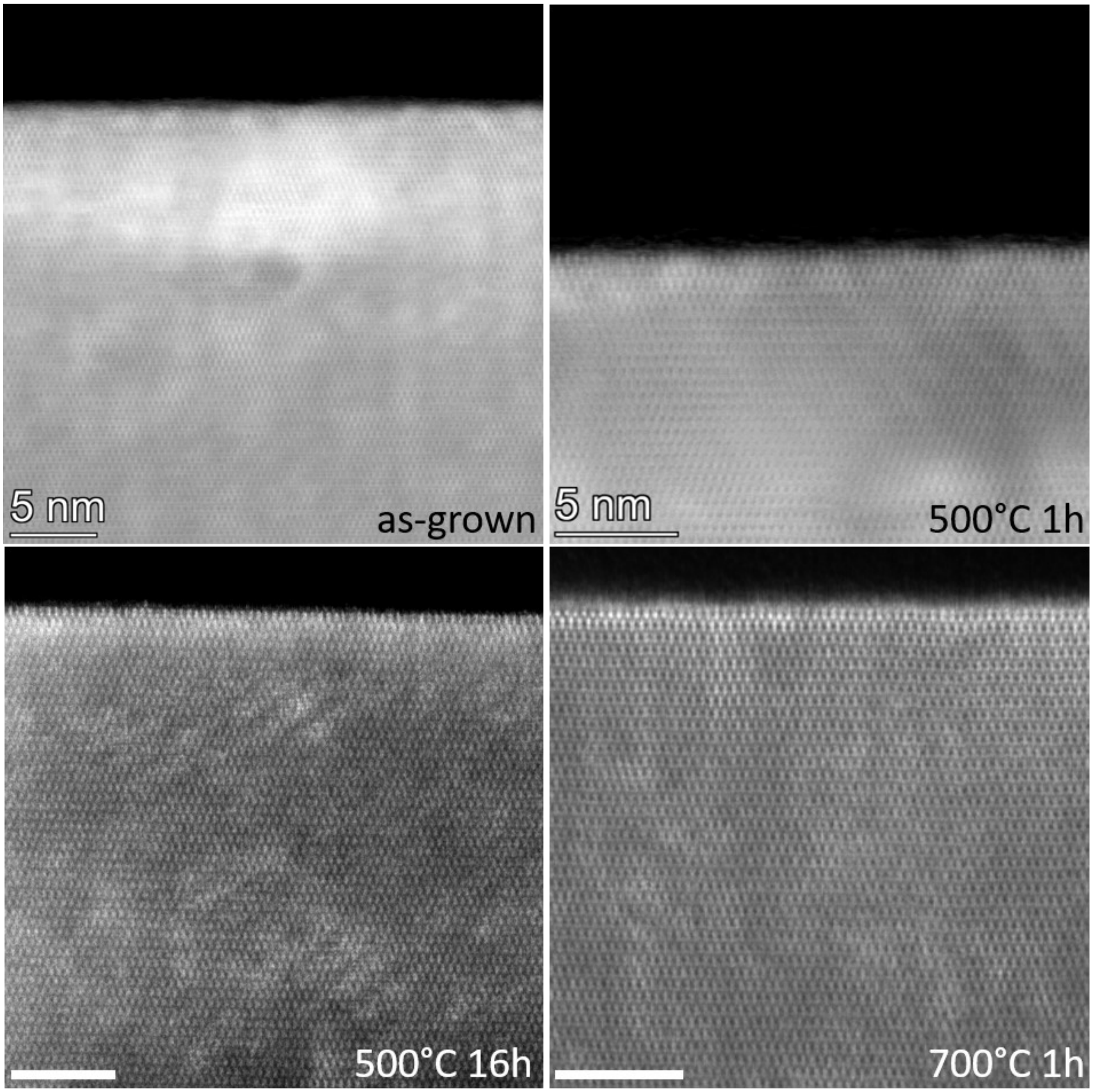

Figure SI6. ADF images utilized for the ADF line profiles displayed in Figure 2d) of the main manuscript. The scale bar always corresponds to 5 nm.

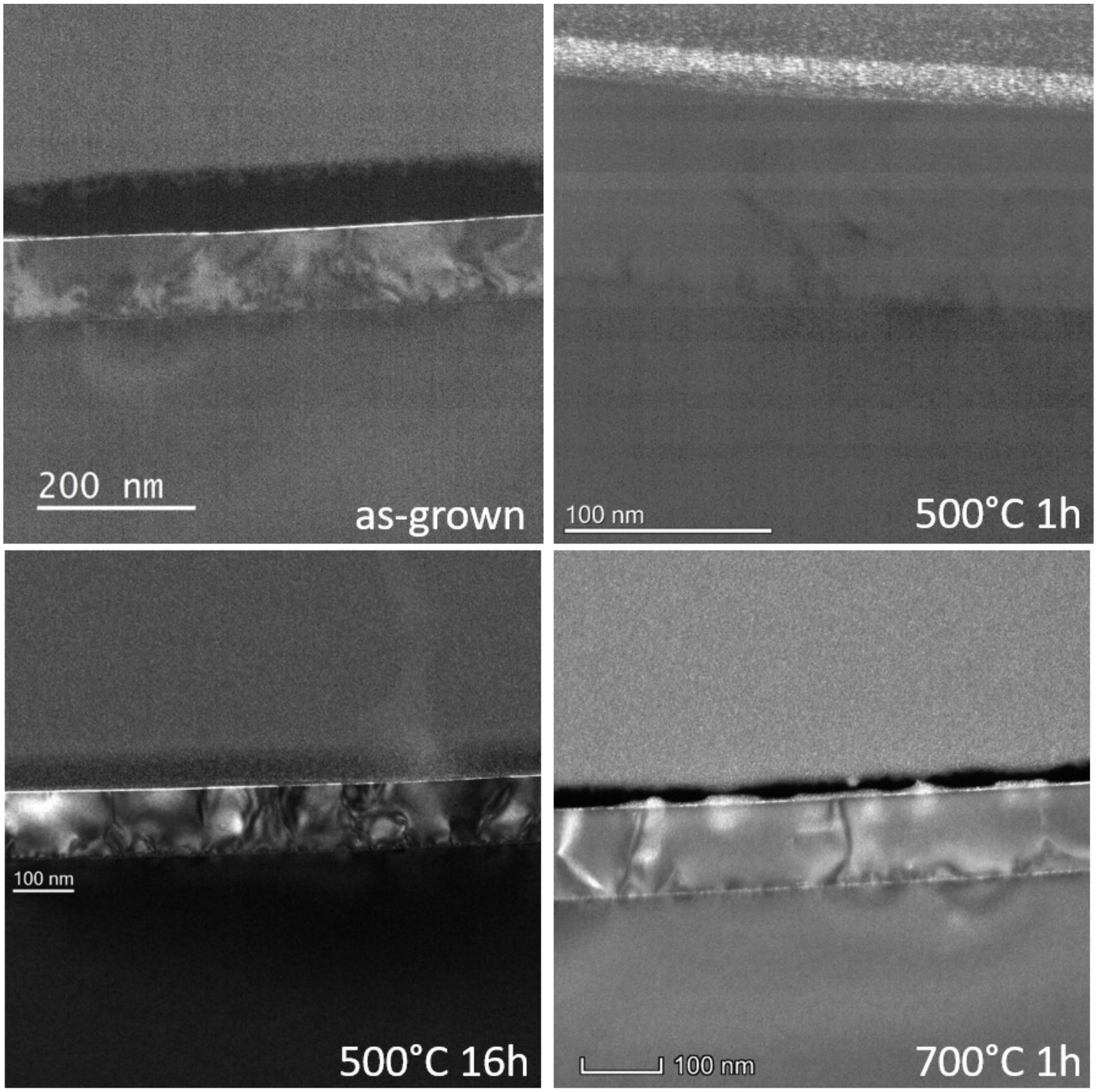

Figure SI7. 002 dark field images of the Anatase epi layers. Note, the thin bright line for all samples besides the 500°C 1h sample, where nearly no intensity is visible at the interface. The residual fanned white background on top of the film stems from the electron beam deposited carbon protective layer deposited during FIB-machining.

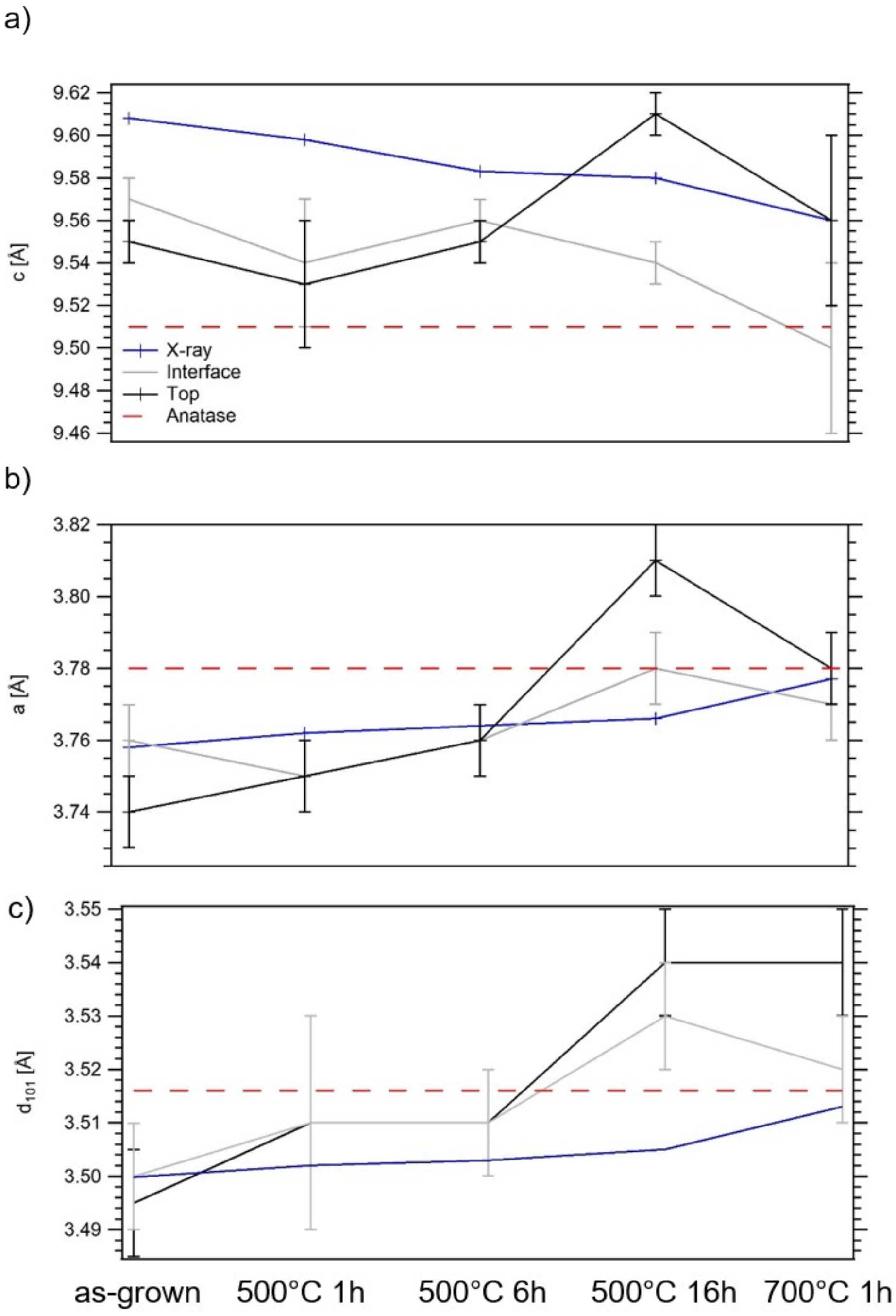

Figure SI8. a) Evaluated evolution of the c axis lattice parameter from out-of-plane XRD (blue) and SAED from the top (black) and bottom (grey) of the anatase film compared to the literature value. b) a axis lattice parameter displayed in the same way as in a). c) Evolution of d_{101} spacing calculated from the a and c axis XRD parameters and determined by SAED from the top and bottom of the anatase layer, respectively.

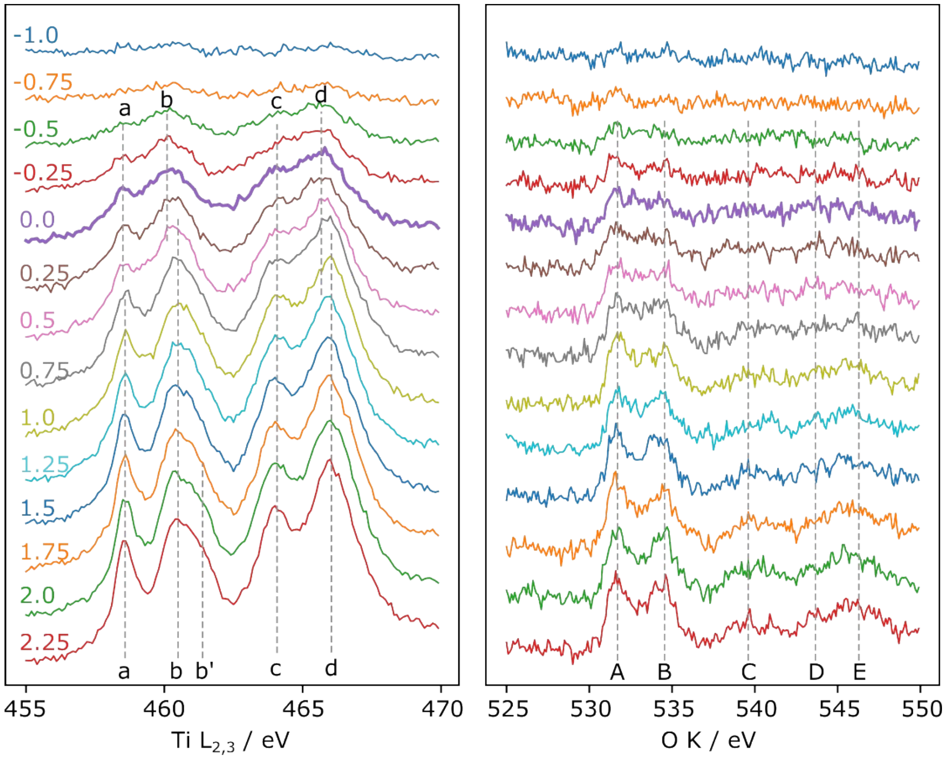

Figure SI9. Spectra extracted from 500C 1h sample in the surface near region. Zero (surface) position is defined as the last recognizable lattice in the simultaneously recorded STEM-ADF image. The spectra fingerprints from ~0.25 inside thin film lattice to -0.5 nm beyond surface represent that of Ti_2O_3 identified in literature,[3] and fine structure fingerprints from about 1.5 nm below the surface into the bulk represent well that of TiO_2 anatase phase in literature.

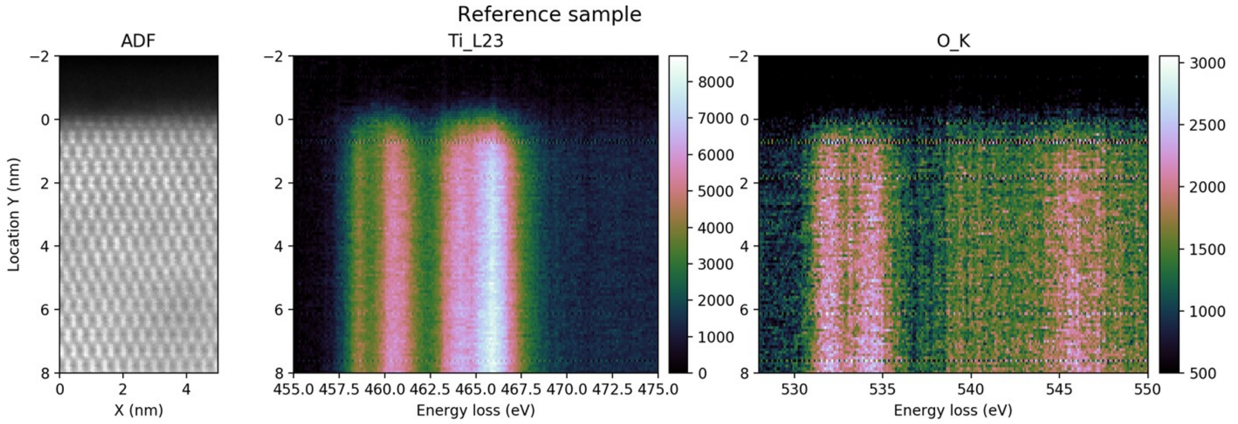

Figure SI10. Simultaneously acquired STEM-ADF image (a) and EELS spectra of Ti-L23 (b) and O-K (c) from the reference sample. Data presented in the same way as in Fig. 5

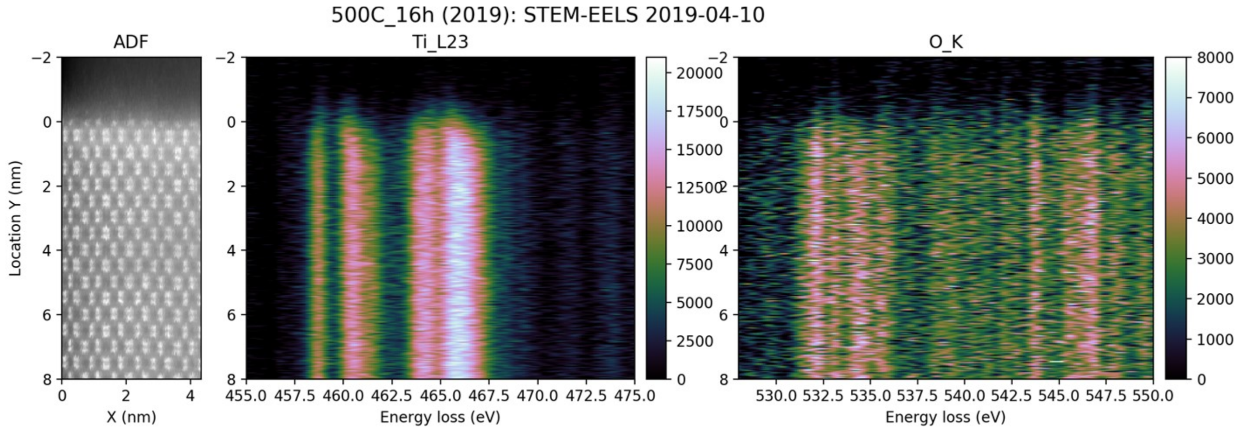

Figure SI11. Simultaneously acquired STEM-ADF image (a) and EELS spectra of Ti-L23 (b) and O-K (c) from the 500C 16h sample. Data presented in the same way as in Fig. 5

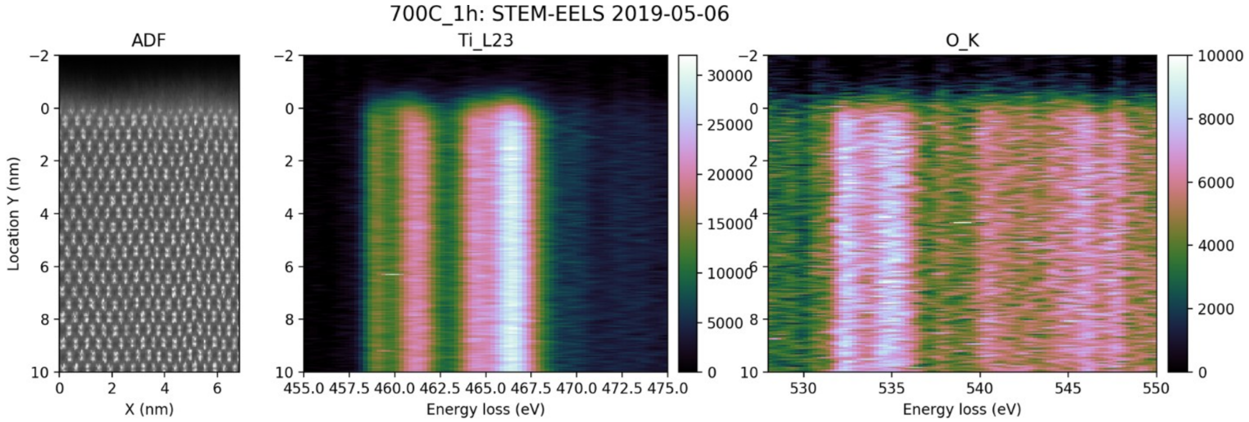

Figure SI12. Simultaneously acquired STEM-ADF image (a) and EELS spectra of Ti-L23 (b) and O-K (c) from the 700C 1h sample. Data presented in the same way as in Fig. 5

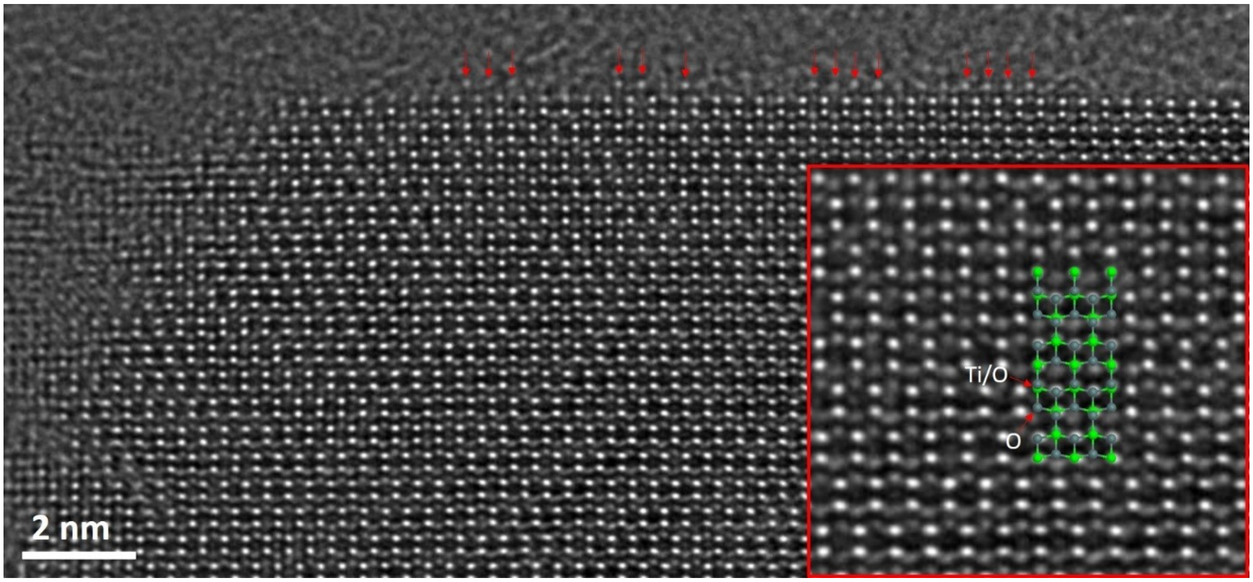

Figure. SI13 Atomically resolved HRTEM image (under negative Cs imaging condition,[4] *contrast directly correlate to atomic positions) of the cross-sectional anatase thin film surface, where dangling Ti/O surface atoms are clearly seen to form discontinuous surface arrangement. Image obtained with the 500C 16h treated sample. TEM specimen estimated to be less than 10 nm.*

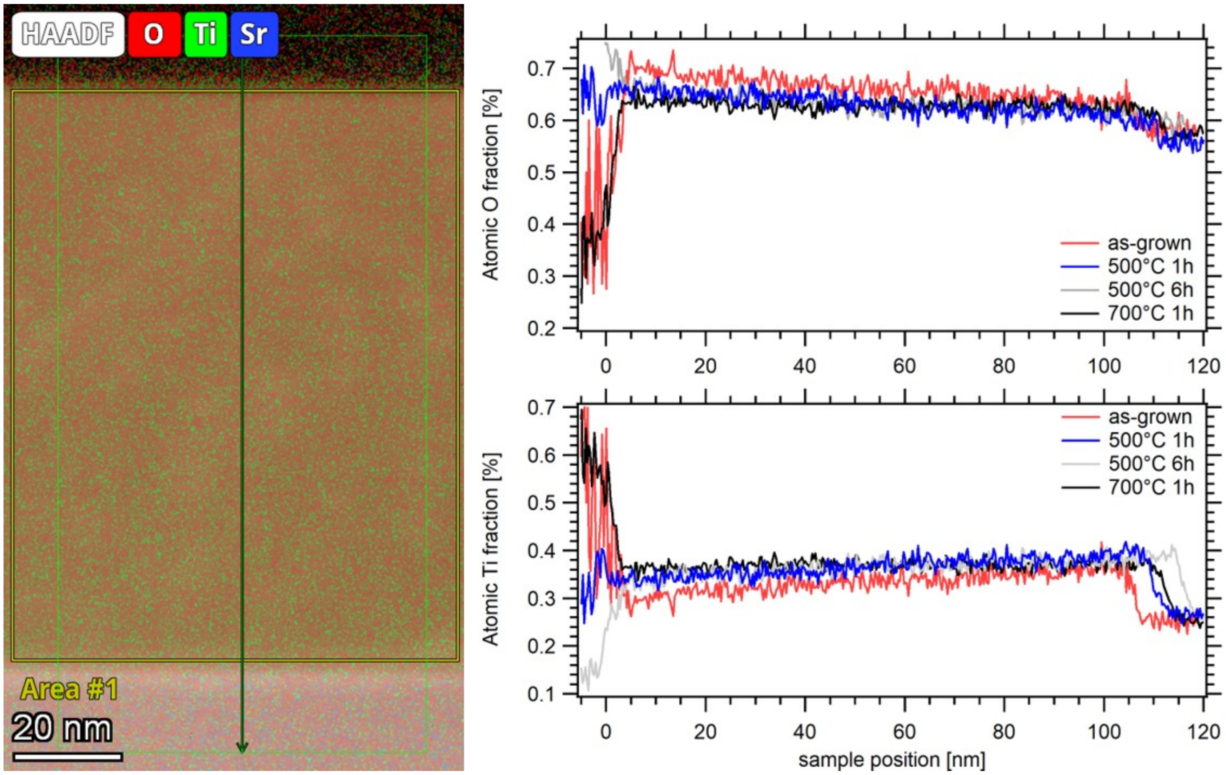

Figure SI14. EDXS map exemplarily shown for the as-grown reference sample (left). Area #1 marks the region from which the average atomic fraction of Ti and O displayed in Table 2 is extracted. The green arrow and box were generated to create line profiles of the O and Ti atomic fraction displayed on the right. Here, the arrow marks the sample position, were the signal is integrated over the width of the box. Above the sample horizon (below 0 nm) noise is recorded, thus this signal is not meaningful. The droop above ~100 nm stems from the interface towards the $SrTiO_3$ substrate.

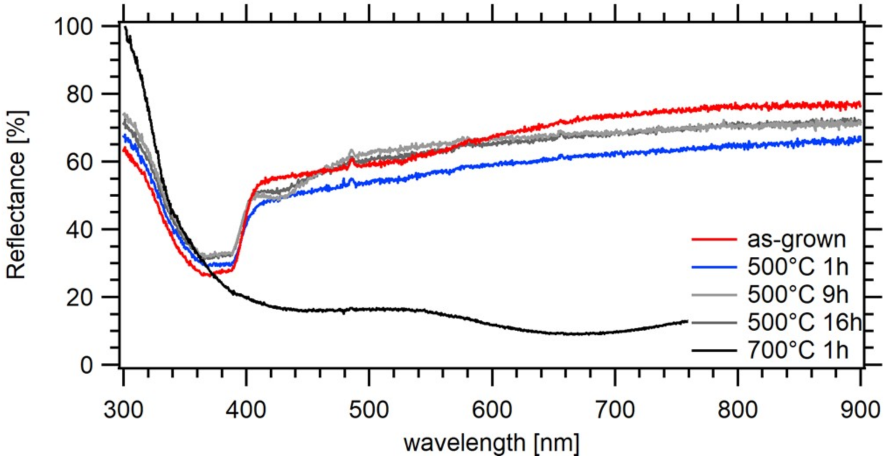

Figure SI15. Diffuse reflectance spectra of the whole measured wavelength regime.

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