Interplay between Steps and Oxygen Vacancies on Curved TiO$_2$(110)

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Supporting Information

ABSTRACT: A vicinal rutile TiO$_2$(110) crystal with a smooth variation of atomic steps parallel to the [1−10] direction was analyzed locally with STM and ARPES. The step edge morphology changes across the samples, from [1−11] zigzag faceting to straight [1−10] steps. A step-bunching phase is attributed to an optimal (110) terrace width, where all bridge-bonded O atom vacancies (Obr vacs) vanish. The [1−10] steps terminate with a pair of 2-fold coordinated O atoms, which give rise to bright, triangular protrusions (S$_t$) in STM. The intensity of the Ti 3d-derived gap state correlates with the sum of Obr vacs plus S$_t$ protrusions at steps, suggesting that both Obr vacs and steps contribute a similar effective charge to sample doping. The binding energy of the gap state shifts when going from the flat (110) surface toward densely stepped planes, pointing to differences in the Ti$^{3+}$ polaron near steps and at terraces.

KEYWORDS: Titanium oxide, STM, rutile, curved crystal, oxygen vacancy, vicinal surface, photoemission

Rutile, the most stable polymorph of titanium dioxide (r-TiO$_2$), is a prototypical, reducible metal oxide. It is applied in many fields ranging from catalysis to memristors. These applications are often enabled by lattice defects, which act as electron donors and convert the otherwise insulating system into an n-type semiconductor. The nature of these defects, as well as their influence on the electronic and chemical behavior of reduced crystals (r-TiO$_2$), has attracted considerable interest. Of particular importance are oxygen vacancies, which donate electrons to the material. Excess electrons in rutile tend to localize at surface and subsurface Ti atoms, forming a Ti$^{3+}$ oxidation state. The localized electron is accompanied by lattice distortions and can be characterized as a small polaron in TiO$_2$ rutile.

Step edges are sites with low atomic coordination and thus chemically and electronically active. Only a few studies on vicinal rutile planes exist, but they reveal the potential of stepped surfaces to further tailor the physical and chemical properties of r-TiO$_2$. Martinez et al. have reported the existence of oxygen vacancies at [1−11] step edges (O$_v$ vacs), as these are easier to form than O$_d$ vacs at terraces. For [1−10] steps, Lutrell et al. have proposed an atomic model without missing oxygen atoms (i.e., no O$_v$ vacs) that still explains the bright features they observe by scanning tunneling microscopy (STM). A systematic study of different vicinal planes that explores the structural stability of both the vicinal surface orientation and the step edge termination, the existence of any characteristic step contributions to electron-doping, or the possible alteration of the Ti$^{3+}$ polaron in the vicinity of steps is still missing.

In this Letter, we demonstrate how a thorough exploration of structural and electronic properties of stepped r-TiO$_2$(110) surfaces can be conveniently performed using curved crystals as samples. Our curved TiO$_2$(110) surface (see Supporting Information (SI)) (c-TiO$_2$(110)) allows a systematic study of stepped r-TiO$_2$(110) surfaces with a tunable density of [1−10]-oriented steps. Using STM we quantitatively analyze the structure and distribution of steps and vacancies as a function of the average deviation (miscut $α$) from the (110) surface. The surface smoothly evolves from wide terraces, containing O$_v$ vacs, toward narrow (110) terraces, depleted of O$_v$ vacs, but with a high density of triangularly shaped protrusions at steps (S$_t$). Such S$_t$-featured steps act as preferred dissociation sites for H$_2$O molecules. Interestingly we find an O$_v$ vacs-free phase with a characteristic step spacing $d_s$, suggesting an energetically

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favorable, vicinal surface orientation. By scanning the photocurrent beam in angle resolved photoemission spectroscopy (ARPES) across the curved sample, we study the spectroscopic signature of the Ti$^{3+}$ polaron, that is, Ti 3d-derived peak in the band gap. The Ti 3d gap state reflects the transition from oxygen-bridge to step-edge-doping across the curved surface through a 110 meV shift in apparent binding energy, which in turn suggests differences in the polaronic relaxation for the two types of trapped electrons. The densities of St protrusions and Obr vacs correlates quantitatively with the gap state intensity, indicating that both triangular features at step edges and Obr vacs at terraces contribute to the crystal doping equally. Density functional theory (DFT) calculations indicate that the electron doping is not an intrinsic property of the step-edge but stems from the presence of Obr vacs. We predict that St protrusions of [1−10] step edges are favorable sites for the formation of Obr vacs in r-TiO$_2$(110).

STM measurements were performed on an Omicron LT-STM head at $T = 80$ K. Tunneling currents $I_t \leq 0.1$ nA and positive sample bias voltages ($V_{sp}$ imaging empty states) ranging from 0.7 to 1.8 V were used. ARPES measurements were performed at a different setup equipped with a hemispherical analyzer (Phoibos150) and a monochromatized Helium 1 ($h\nu = 21.2$ eV) source with an overall energy/angle resolution of 40 meV/0.1°. All experiments were done using a rutile single crystal curved around the [110] symmetry direction (BihurCrystal Ltd.), as schematically depicted in Figure 1a. The curving process leads to a smooth $\alpha = \pm 12^\circ$ miscut variation around the (110) surface, that is, a variable density $1/d$ ($d$ being the step spacing) of monatomic ($h = 3.25$ Å, $d = h/sin \alpha$) steps oriented parallel to the [1−10] direction.

Argon sputtering (1 keV) and annealing (up to 1000 K) cycles both cleaned and reduced the c-TiO$_2$(110) crystal surface. Sputtering was performed parallel to the steps, which prevents damaging the stepped regions. The selected annealing temperature was sufficient to heal the sputter-damage. We roughly define three different levels of reduction, judged from the characteristic color of the sample. Starting from a transparent crystal, a sufficiently clean and conducting surface was achieved with $\sim$5 sputtering–annealing cycles. This defines
the slightly reduced sample, characterized by a faint blue color. The intermediate (blue crystal) and the strongly reduced (dark crystal) stage were reached with 30 and 60 sputtering–annealing cycles, respectively. The characteristic 1 × 1 low energy electron diffraction (LEED) pattern for the unreconstructed sample is shown in Figure 1b. Further sputter–annealing beyond 100 cycles led to a 2 × 1 surface reconstruction. With LEED, we measured the step spacing at each sample position, which determines the local crystallographic plane. STM images were quantitatively analyzed through an automated routine, which rendered the average terrace width d and its standard deviation σ (see SI) at each sample position. All STM images presented here are high-pass filtered, which enhances the contrast at the terraces.

The smoothly varying step density 1/d of the c-TiO2(110) sample is directly visualized in a LEED “z-scan”, shown in Figure 1b. In such a z-scan the sample is displaced vertically (z-scale in Figure 1) in front of the 0.3 mm broad electron beam. The example on top of Figure 1b shows the pattern taken at z = 4 mm (α = 8°); it exhibits the spot-splitting characteristic for stepped surfaces. The dotted box indicates a selected line over this LEED pattern, crossing the (−1−1), (−10), and (−11) spots. The z-scan in the bottom of Figure 1b is built with individual spot line profiles taken in Δz = 0.5 mm steps across the surface. It shows a linear variation of the spot splitting at both sides of the crystal, reflecting a linear change in 1/d.

Despite the extensive sputter–annealing, the curved crystal surface remained stable and continued to exhibit a position-dependent terrace-step structure. The STM images in panels correspond to the strongly reduced surface and are taken at the three characteristic positions marked in Figure 1a. At the (110)-oriented center of the crystal the striped pattern reflects the presence of the alternating rows of bridge-bonded O and Ti atoms, better seen in the zoomed area of Figure 1g. The Obr vacs appear as bright features bridging Ti rows in STM images of r-TiO2(110). The morphology of step edges varies across the c-TiO2 sample in the way qualitatively sketched in Figure 1c. At relatively low step densities [Figure 1e], zigzag edges are observed with long segments parallel to [110] and [−111]. Such [111]-type steps are energetically favorable in rutile TiO2(110), as compared to [1−10] steps. At large step densities (1/d), the zig-zagging is reduced and steps mostly align parallel to the [−1−10] direction, as shown in Figure 1f.i. In all cases, step edges exhibit triangularly shaped protrusions (S1 protrusions) at positive STM bias. At [1−11] steps, bright features have been previously associated with vacancies (O vacs). In contrast, S1 protrusions at [1−10] steps have been linked to the two-fold-coordinated bridge oxygen atoms (Ox) that terminate the armchair edges, see the sketch in Figure 1h. Although the oxygen coordination is two-fold also in terraces, here the Ox atoms are bound to under-coordinated Ti atoms, which results in a larger contribution to the empty states image in STM (see Figure S9 in the Supporting Information file), as compared to Obr atoms in terraces. Because the density of Ox sites is selectively tuned across the curved surface, an important question is whether such Ox atoms are active sites at the TiO2(110) surface, that is, whether they exhibit enhanced chemical affinity to adsorbates and whether and how they contribute to the doping charge of the crystal.

By sputter–annealing, we can transform the stoichiometric to the reduced stage of the crystal that results in a change in the number of Obr vacs, as illustrated in Figure 2a,b. In contrast, the reduction process has a smaller effect on the density of triagonally shaped protrusions, which are already visible at the slightly reduced sample [Figure 2a]. Obr vacs have been reported to migrate from terraces to steps, leading to Obr vac-depleted terrace fringes in the proximity of [1−11]-oriented steps. Such Obr vac migration effect supports our results displayed in Figure 2. Here we statistically evaluate the distance from the step edge to the nearest Obr vacancy in ~10 STM images of the reduced surface. Assuming that both step edges are equivalent, the peak at ~1.6 nm suggests that the density of Obr vacs will be very low in terraces with a width below dmin = 2 × 1.6 = 3.2 nm. Finally, oxygen vacancies of terraces and S1 features are tested against water adsorption at room temperature in Figure 2d. Water molecules dissociate in an analogous way at Obr vacs of terraces and [1−10] steps, suggesting their similar reactive nature.

A statistical analysis of the terrace size in step arrays performed across the curved crystal provides key insights into the interplay between steps and vacancies on stepped rutile TiO2(110). This analysis delivers probability histograms for the local terrace width d, such as those shown in the insets of Figure 1e,f. Note that the histogram of Figure 1e (strongly reduced surface) shows a maximum probability at around d ∼ 2.5 nm. This is significantly narrower than the mean terrace width d̃ at that sample position. This observation suggests that steps tend to group, forming bunches with a critical spacing dc. It is straightforward to deduce such a step-bunching effect in the intensity plot of Figure 3a. Here the image is built with all terrace width distribution histograms taken across the curved surface and plotted against the corresponding average terrace width d (vertical axis). The thick d = d line would mark the maximum for a symmetric histogram, that is, the probability maximum expected for a simple, periodic step superlattice. In Figure 3a, we observe that for step arrays with average terrace width up to d ∼ 3 nm the histogram maximum lies on the d = d line. In contrast, for arrays with larger d the maximum deviates from the d = d line at a constant d = 2.8 nm (dotted line). Note that d falls right below the minimum dmim = 3.2 nm width.
by surface charge neutrality in ZnO,23,24 as well as the herringbone in Au(111)21 and the 7 × 7 in Si(111),22 or a large entropic contribution to the surface free energy.20

The existence of the stable, Obr vace-free stepped phase that allows Obr vacs within terraces. Therefore, for \( \tilde{d} > d_c \) the stepped surface exhibits both Obr vace-filled \( (d > d_c) \) terraces and Obr vace-free \( (d < d_c) \) bunches.

The equilibrium shape of the step lattice results from the interplay of different interactions, mostly of elastic origin, but also of other nature, such as entropic, electrostatic, and electronic.20 Steps lead to local crystal lattice relaxations, which extend several nanometers in all directions. Elastic fields of contiguous steps overlap, leading to repulsive, \( \propto 1/d^2 \) interactions. When no other interactions exist, step–step repulsion results in periodic step arrays. Step bunching reveals the presence of other contributions to the energy balance. This is the case of facetting induced by surface reconstructions, such as the herringbone in Au(111)21 and the 7 × 7 in Si(111),22 or by surface charge neutrality in ZnO,23,24 as well as the bunching triggered by electric-dipole-like attractive interactions between steps in Cu(100)25 or GaAs(001).26 In the stepped TiO2(110) system analyzed here, the structural distortions caused by Obr vacs necessarily alter the surface free energy at (110) terraces. The existence of the stable, Obr vace-free stepped phase suggests that Obr vacs increase such elastic energy, such that a Obr vace-free phase with \( d_c \approx 2.8 \) nm is promoted. However, the slightly reduced surface with a much lower density of Obr vacs also exhibits step bunching [Figure 3a], although with slightly wider critical terrace \( 
\tilde{d} \approx 3.7 \) nm. In the absence of Obr vacs at terraces, or any other kind of structural defects or reconstructions, a step bunching phase is explained by attractive interactions between steps. Therefore, a more complex scenario appears to be present, where both attractive step–step interactions and Obr vacancies enter the elastic energy balance, leading to step bunching at \( d_c \) values that depend on the density of Obr vacancies.

Terrace-width histogram plots like these of Figure 3 contain further information. As recently shown for a c-Pt(111) crystal,27 they allow visualizing the universal transition from entropic to elastic interactions in step arrays.20 In fact, at high step densities strong repulsive \( 1/d^2 \)-interactions define straight edges, but at low densities steps do not interact with each other so effectively and the step energy dictates the edge morphology. Non-interacting steps are allowed to twist, exhibiting, for example, the favorable [1−11]-like orientations forming a zigzag in c-TiO2(110), or a round profile in c-Pt(111), which reflects minor energy variations among distinct facet orientations in metals. In either case, c-TiO2(110) or c-Pt(111), the terrace size distributions are rather symmetric, Gaussian-like in dense step lattices (interacting steps) but develop a larger asymmetry or tail toward big \( d \) values in sparse lattices. This tail is clearly visible in both plots of Figure 3. It reflects that there is a large number of step atom configurations of similar energy, rendering a large entropic contribution to the surface free energy.20

The doping effect caused by steps featured with \( \tilde{d} \) triangular protrusions and Obr vacs is tested through the Ti 3d gap state, which is the spectroscopic signature for all electron-donating defects in TiO2.4,24,25 ARPES spectra are analyzed as a function of the step density (z-scan, as in Figure 1b) and the reduction level (see Figure 4). To clearly separate Obr and step contributions, we focus on the slightly reduced surface where the presence of oxygen defects is lowest. For the more stepped part of the sample, the surface is practically free of Obr vace, whereas the center has an irrelevant contribution of steps. Figure 4a corresponds to a z-scan of the Ti 3d gap state from the center (top) to the edge (bottom) of the slightly reduced sample, under normal emission conditions (\( \theta = 0^\circ \)). The persistence of the Ti 3d gap state is consistent with the fact that both Obr vacs of terraces and steps are electron-donating entities. Yet an energy shift is observed in the gap state from the center to the edge of the crystal. Background-subtracted spectra taken at the center and the densely stepped region are directly overlaid (Figure 4a bottom). A clear \( \Delta E = 110 \pm 20 \) meV shift to higher binding energies is found from the (110) plane \( (E = −0.82 \) eV) to the stepped surface \( (E = −0.93 \) eV). A close view at the corresponding O 2p evolution discards changes in band
bending as a possible reason for the observed shift, as discussed in the SI. An energy shift in the gap state peak of the (110) plane could be expected at distinct Ti environments, such as steps and defects, which imply different lattice distortion (polaron). It can also arise due to the different coordination of Ti atoms at the step edge, which leads to an effectively different valence state. For example, for the 2 × 1 phase with nominal Ti₂O₃ composition, that is, lower Ti coordination to O atoms, a 120 meV shift to higher binding energy has been reported.²⁸

To quantify the variation of the doping charge in the curved crystal, we analyze the photoemission intensity of the Ti 3d gap state for this purpose, a wide emission angle integration is required, given the large angular variation of the gap state intensity in ARPES, as discussed in detail in the SI. In Figure 4b, the Ti 3d gap states for the curved crystal center (z = 0) and the highly stepped edge (z = 5 mm) [points d and f in Figure 1a, respectively] are compared, at different degrees of surface reduction. Data correspond to the full integration of the emission plane accessible in the experiment, namely Δθ = −10° to +70° in the [1−10] direction parallel to surface steps, and Δβ = ±12° in the [00−1] perpendicular direction (cf. Figure S6). The step-related energy-shift persists, but it is smaller at strongly reduced surfaces. The latter is consistent with the widely accepted picture that the polarons first occupy special sites (at the step edges in the present case), followed by regular lattice positions.²⁹

The advantage of the curved surface is that the very same reduction process is applied to all surface orientations at once. Thus, it is remarkable to observe that the gap state shows minor intensity differences from flat to stepped surfaces at any reduction stage. This indicates that the total doping charge, originating from both, Obr vacs and St steps, remains constant across the curved surface. In Figure 4c, we study the correlation between the concentration of Obr vacs and S triangles and the gap state intensity. Red and blue data points represent the density (in monolayers, ML) of Obr and S triangles, measured directly from STM images as a function of the terrace size d. White dots correspond to the gap state intensity (area under the peak), averaged to the photon intensity over selected ARPES z-scans of the reduced surface. Error bars reflect the intensity variation between stepped and nonstepped areas, which may vary by 10%, depending on the emission angle integration (see SI). The concentration of triangles follows the step density variation 1/d (blue line), meaning that such features saturate step edges at any terrace width. The dotted portion of the line indicates that triangles cannot be resolved in large area images, which are needed to properly quantify STM data at low step densities. By contrast, the concentration of Obr vacs is fitted with the empirical function Obr (d) = 1/D₀ − 1/d (red line), which reflects in the most simple way the qualitative observations of Figures 2 and 3, namely, the existence of Obr vac-free areas close to step edges (also 1/d dependent) and a critical terrace size below which Obr vacs vanish (1/D₀). The best fit is obtained for D₀ values around 1.9 nm, that is, slightly below the d̅ₐ = 2.8 nm value deduced from Figure 3.

The most interesting conclusion from Figure 4c is that the direct sum of the fitting lines for Obr vacs and S triangles leads to almost the complete cancellation of 1/d dependence and hence to a constant line that fits the photoemission data on top. This means that every S triangle at a step edge donates to the crystal the same electronic charge as one Obr vacancy on a (110) terrace. The question that arises is which physical entity donates the doping charge at the step edge. We have theoretically analyzed the role of steps as electron dopants and found out that neither the low-coordinated Ti atoms nor the O atoms at the step edges introduce any additional states inside the gap, that is, they do not donate any electrons to the crystal. We thus analyzed the interplay between the two-fold oxygen vacancies and the step edges (see SI). We should notice that the presence of one Obr vacancy per each S triangle could directly explain the STM/ARPES results of Figure 4.

Interestingly, our calculations indicate that Obr vacancies have lower formation energy at the upper corner of the armchair unit cell, as compared to Obr vacancies in terraces. This suggests that, as observed in [1−11] steps, Obr vacancies migrate to step edges, saturating them at a sufficient reduction stage (Figure 4). On the other hand, as shown in Figure S9 of the SI file, the presence of Obr vacancies at step edges does not considerably alter the STM image due to the strong contribution from the O atoms and the low coordinated Ti atoms at the step edge. In summary, the curved-crystal approach allows us to rationally investigate the interplay between steps and Obr.
vacancies in stepped rutile TiO₂. Such crystals are remarkably stable; the step-terrace structures survives typical sputter-annex cleaning cycles and even heating at atmospheric pressures (see SI). The STM analysis shows a smooth evolution from flat surfaces with abundant bridge-bonded O vacancies to densely stepped surfaces, featuring triangular step-edge protrusions. A step-bunching phase made of vacancy-free terraces is observed to segregate at relatively sparse step arrays, suggesting that O vacancies in stepped r-TiO₂(110) interfere with the elastic/entropic step interaction, characteristic of Cabailh, G.; Chen, Q.; Fisher, A. J.; Hofer, W. A.; Thornton, G. Natl. Acad. Sci. U. S. A. M.; Van de Walle, C. G.; Kresse, G.; Diebold, U. Hammer, B.; Besenbacher, F. Hansen, J. Ø.; Matthiesen, J.; Blekinge-Rasmussen, A.; Lægsgaard, E.; financial support by the Deutsche Forschungsgemeinschaft through SFB 1083 “Structure and Dynamics of Internal Interfaces”.

Additional information on the curved sample cleaning and reduction in UHV, STM, and ARPES analysis, water adsorption on strongly reduced surfaces, and DFT simulations of vacancies at step edges. (PDF)

The authors declare no competing financial interest.

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