

# The Role of Interstitial Sites in the Ti3d Defect State in the Band Gap of Titania

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Titanium dioxide (TiO<sub>2</sub>) has a number of uses in catalysis, photochemistry, and sensing that are linked to the reducibility of the oxide. Usually, bridging oxygen (O<sub>br</sub>) vacancies are assumed to cause the Ti3d defect state in the band gap of rutile TiO<sub>2</sub>(110). From high-resolution scanning tunneling microscopy and photoelectron spectroscopy measurements, we propose that Ti interstitials in the near-surface region may be largely responsible for the defect state in the band gap. We argue that these donor-specific sites play a key role in and may dictate the ensuing surface chemistry, such as providing the electronic charge required for O<sub>2</sub> adsorption and dissociation. Specifically, we identified a second O<sub>2</sub> dissociation channel that occurs within the Ti troughs in addition to the O<sub>2</sub> dissociation channel in O<sub>br</sub> vacancies. Comprehensive density functional theory calculations support these experimental observations.

Titanium dioxide (TiO<sub>2</sub>), or titania, is used in a number of technological areas, including heterogeneous catalysis, photocatalysis, solar cells, gas sensors, waste remediation, and biocompatible materials. In its stoichiometric form, titania is an inert wide-band gap insulator; however, its applications are enabled by excess electrons originating from the defect state that is located within the band gap of reduced titania (TiO<sub>2-x</sub>). Understanding the origin of the defect state is important for improving or expanding the scope of titania-based systems for specific applications. For example, the enhanced catalytic activity of titania-supported gold nanoparticles is coupled to local properties at the interface between gold and reduced titania (1–4).

Conventionally, the Ti3d derived state in the band gap (5–7) at ~0.85 eV below the Fermi level (E<sub>F</sub>) has been fully ascribed to bridging oxygen (O<sub>br</sub>) vacancies, because, in an ionic picture, the two excess electrons per O<sub>br</sub> vacancy may be transferred to neighboring Ti atoms (5, 6, 8–11). This hypothesis was proposed more than three decades ago based on ultraviolet photoelectron spectroscopy (UPS) and low-energy electron-diffraction measurements on the TiO<sub>2</sub>(110)–(1 × 1) surface (8), and has been generally accepted for years (5, 6, 9, 11). In the UPS studies, this proposed O-vacancy model has largely been based on experimental observations that the defect state can be eliminated by O<sub>2</sub> exposure (8, 12, 13). Further possible support for the O-vacancy model came from scanning tunneling microscopy (STM) (14–17) and atomic force microscopy (18) studies, where O<sub>br</sub> vacancies have been clearly identified

on TiO<sub>2</sub>(110). Although most first-principles density functional theory (DFT) calculations have not reproduced the experimentally observed state in the band gap (11), numerous theoretical papers still favor the O-vacancy model (6, 11).

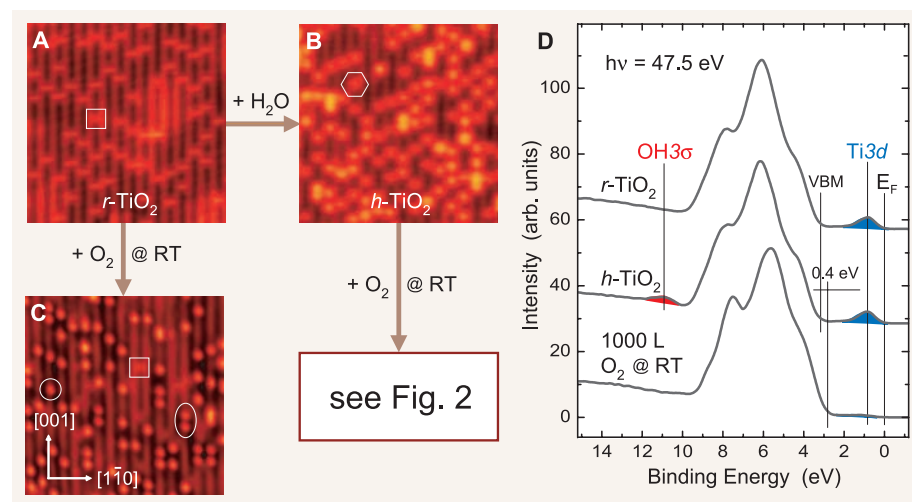
Nevertheless, the importance of Ti interstitials in rutile TiO<sub>2</sub>(110) crystals has been noted. For example, the reoxidation of sputtered TiO<sub>2</sub>(110) surfaces via vacuum annealing has been explained by Ti interstitial diffusion into the bulk (19–21). Similarly, when a reduced TiO<sub>2</sub>(110) crystal is exposed to O<sub>2</sub> at elevated temperatures, diffusion of Ti interstitials to the surface has been

reported (2, 22–24). Therefore, in addition to O vacancies, Ti interstitials must also be considered as defect sites that may influence and even dictate the surface chemistry of titania.

By means of high-resolution STM and photoelectron spectroscopy (PES) measurements in conjunction with DFT calculations, we have systematically explored the origin of the Ti3d defect state in the band gap. We found that the gap state remains almost unchanged on surfaces where the O<sub>br</sub> vacancies (or bridging OH groups) have been removed. To explain this finding, we propose that the gap state mainly stems from surplus Ti atoms in the near-surface region, most likely on interstitial sites. In addition to an O<sub>2</sub> dissociation channel in O<sub>br</sub> vacancies, we discovered a non-vacancy-related O<sub>2</sub> dissociation channel that occurs within the Ti troughs.

The TiO<sub>2</sub>(110)–(1 × 1) surface consists of alternating rows of fivefold-coordinated Ti (5f-Ti) atoms (the Ti troughs) and protruding, twofold-coordinated O<sub>br</sub> atoms. As bulk Ti atoms in stoichiometric rutile, the Ti atoms underneath the O<sub>br</sub> atoms are sixfold-coordinated. Ion-sputtering and vacuum-annealing the TiO<sub>2</sub>(110) crystal results in a reduced n-type semiconductor, with a bulk conductivity that allows the use of STM and other electron spectroscopy techniques. Consistent with previous findings (6), the STM images (Fig. 1) of the TiO<sub>2</sub>(110) surface are dominated by electronic effects; that is, the bright rows correspond to the Ti troughs, whereas geometrically protruding O<sub>br</sub> atoms appear as the dark troughs in the STM images (6).

A high-resolution STM image recorded on a clean reduced TiO<sub>2</sub>(110) surface [*r*-TiO<sub>2</sub>(110)]



**Fig. 1.** STM images (105 by 105 Å) of *r*-TiO<sub>2</sub>(110) (A), *h*-TiO<sub>2</sub>(110) (B), and a RT O<sub>2</sub>-saturated TiO<sub>2</sub>(110) surface (C) acquired using a sample in a reduction state corresponding to an O<sub>br</sub>-vacancy density of 11.4 ± 0.3% MLs. Symbols indicate O<sub>br</sub> vacancies (square), capping H atoms (hexagon) in the O<sub>br</sub> rows, and O<sub>at</sub> adatoms (circle), as well as pairs of next-nearest O<sub>at</sub> adatoms (ellipse) in the Ti troughs. STM images were collected with a tunneling current (*I*<sub>t</sub>) ≤ 0.1 nA and a tunneling voltage (*V*<sub>t</sub>) = 1.2 V. Directions throughout the paper are identical to those indicated in (C). Corresponding PES valence-band spectra are shown in (D). PES spectra and STM images were recorded at sample temperatures between 100 and 130 K. The position of the valence-band maximum is indicated by VBM and the Ti3d defect state is observed within the ~3.1-eV-wide band gap.

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(Fig. 1A) shows faint protrusions that appear between the bright Ti troughs and that correspond to  $O_{br}$  vacancies in the  $O_{br}$  rows (14–17). Starting from an  $r$ - $TiO_2(110)$  surface, we studied the effect of hydration by letting water dissociate in the  $O_{br}$  vacancies (Fig. 1B). The brighter protrusions in the  $O_{br}$  rows appearing on the resulting hydrated  $TiO_2(110)$  surface [ $h$ - $TiO_2(110)$ ] originate from capping H atoms or, in an alternative notation, from  $OH_{br}$  groups (14–17). In the PES valence-band spectra corresponding to  $r$ - and  $h$ - $TiO_2(110)$  (Fig. 1D), the only obvious difference is the  $OH3\sigma$  feature at a binding energy (BE) of  $\sim 10.8$  eV that is evident in the valence band after hydration (12). The  $Ti3d$  defect state at  $\sim 0.85$  eV below  $E_F$  is only minimally affected by hydration, in spite of the complete absence of  $O_{br}$  vacancies on  $h$ - $TiO_2(110)$ .

In an attempt to “heal” the  $O_{br}$  vacancies on  $r$ - $TiO_2(110)$  without producing capping H atoms on the  $O_{br}$  rows, we studied the interaction of  $O_2$  with clean  $r$ - $TiO_2(110)$  at room temperature (RT). The number of  $O_{br}$  vacancies decreased after the  $O_2$  exposure (Fig. 1C), and a number of bright spots appeared simultaneously on the Ti troughs, some of which are next-nearest neighbors. Based on previous  $O_2$  interaction experiments (3, 14, 25), the spots in the Ti troughs are assigned to O adatoms that reside on top of 5f-Ti atoms ( $O_{ot}$ ). However,  $O_2$  exposure at RT does not lead to the healing of all the  $O_{br}$  vacancies, even in the case of saturation (26). In the valence-band spectrum corresponding to the  $O_2$ -exposed  $TiO_2(110)$  surface, one feature is the strongly suppressed defect state at  $\sim 0.85$  eV (Fig. 1D). In addition, compared with the spectra for  $r$ - and  $h$ - $TiO_2(110)$ , the dominating features between BEs of  $\sim 3$  and  $\sim 9.5$  eV [primarily  $O2p$ -derived (5, 7, 12, 27)] were found to be shifted by  $\sim 0.4$  eV toward  $E_F$ .

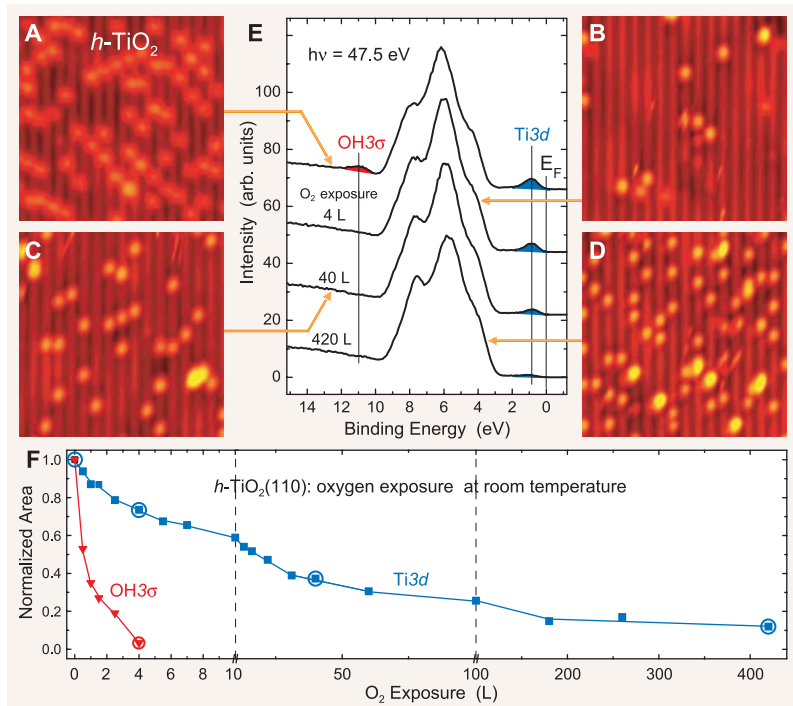
Both of these adsorption experiments, hydration of  $r$ - $TiO_2(110)$  as well as oxidation of  $r$ - $TiO_2(110)$  at RT, raise questions about the origin of the  $Ti3d$  defect state. In the case of the  $h$ - $TiO_2(110)$  surface, the assignment of the defect state is hampered because of capping H atoms, which also could lead to a state in the band gap (10). Because  $O_2$  exposure at RT to  $r$ - $TiO_2(110)$  leads to a surface with  $O_{ot}$  adatoms and residual  $O_{br}$  vacancies, and not to a  $TiO_2(110)$  surface that is characterized by perfect  $O_{br}$  rows as was previously assumed (8), this experiment also does not reveal the origin of the defect state. In order to assign the  $Ti3d$  defect state,  $TiO_2(110)$  surfaces need to be prepared that are characterized by perfect  $O_{br}$  rows without  $O_{br}$  vacancies and capping H atoms, and by Ti troughs without  $O_{ot}$  adatoms.

Motivated by the observation that the capping H atoms on the  $O_{br}$  rows can be reacted off via reaction with  $O_2$  (28), we exposed  $h$ - $TiO_2(110)$  surfaces to  $O_2$  at RT (Fig. 2). As revealed by the STM images depicted in Fig. 2, A to D, it is possible to react off all capping H atoms from the  $O_{br}$  rows and create a  $TiO_2(110)$  surface with perfect  $O_{br}$  rows. However, for  $O_2$  exposures

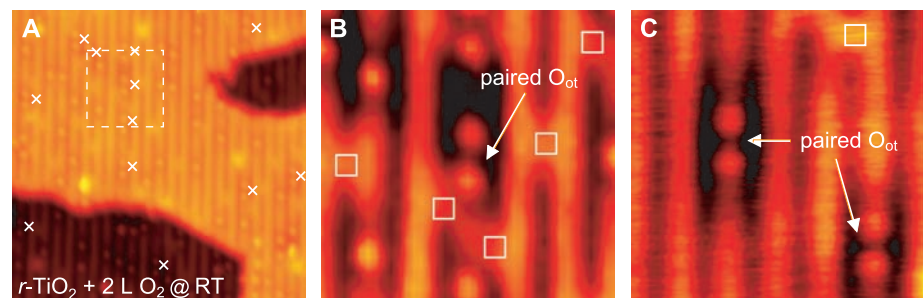
greater than an optimum value, all of the capping H atoms were removed, but additionally, new surface species with an elongated shape appeared within the Ti troughs (Fig. 2, C and D).

We considered the PES results acquired with surface preparations identical to those in the STM experiments and focused on the  $OH3\sigma$  feature at  $\sim 10.8$  eV and on the  $Ti3d$  defect state (Fig. 2E). The  $OH3\sigma$  feature was completely attenuated after an  $O_2$  exposure of 4 Langmuirs (L 1L =  $1.33 \times 10^{-6}$  mbar-sec, whereas much higher exposures were required to minimize the  $Ti3d$  defect state

(420 L). For clarity, the evolutions of the  $Ti3d$  defect state and the  $OH3\sigma$  feature are shown in Fig. 2F in greater detail, and the development of the  $OH3\sigma$  feature for  $O_2$  exposures of  $\leq 4$  L is shown in fig. S1 (26). One observation from Fig. 2F is that for 4-L  $O_2$  exposure, where the  $TiO_2(110)$  surface is characterized by perfect  $O_{br}$  rows and essentially without capping H atoms, the  $Ti3d$  defect state was only slightly attenuated. In complete contradiction to the conventionally accepted O-vacancy model, the PES valence spectra in Fig. 2 reveal that the  $Ti3d$  defect state



**Fig. 2.** (A to D) STM images (105 by 105 Å) of an  $h$ - $TiO_2(110)$  surface that was exposed to increasing amounts of  $O_2$  at RT. For these experiments we used a  $TiO_2(110)$  crystal with an  $O_{br}$ -vacancy density of  $5.5 \pm 0.2\%$  MLs. (E) Selected PES valence-band spectra recorded on an  $h$ - $TiO_2(110)$  surface that was exposed to  $O_2$  at RT. Arrows indicate the representative STM images. For the PES experiments, a  $TiO_2(110)$  crystal was used with an  $O_{br}$ -vacancy density of  $11.4 \pm 0.3\%$  MLs. (F) Normalized integrated intensities of the  $OH3\sigma$  (red) and  $Ti3d$  (blue) features for  $O_2$  exposures up to 420 L from PES spectra; circles indicate intensity values that were obtained from the spectra shown in (E).



**Fig. 3.** STM results illustrating the reaction of  $O_2$  with  $r$ - $TiO_2(110)$  at RT. (A) STM image (155 by 155 Å) acquired after 2-L  $O_2$  exposure. White crosses indicate pairs of next-nearest  $O_{ot}$  adatoms. (B) Zoom-in STM image (38 by 38 Å) of the area indicated by the dashed white square in (A). White squares indicate  $O_{br}$  vacancies. (C) Zoom-in STM image (38 by 38 Å) acquired after 200-L  $O_2$  exposure at RT. Before the  $O_2$  exposure, this  $r$ - $TiO_2(110)$  crystal was characterized by an  $O_{br}$ -vacancy density of only  $\sim 1.7\%$  MLs. STM images were acquired at temperatures between 110 and 130 K.



is caused by neither  $O_{br}$  vacancies nor capping H atoms on the  $O_{br}$  rows. Rather, we will show in the following that the  $Ti3d$  defect state can be directly correlated with the existence of near-surface Ti interstitial defect sites. Within this model, electronegative adsorbates, such as those shown in Fig. 2, C and D, are stabilized on  $TiO_2(110)$  surfaces with perfect  $O_{br}$  rows through charge transfer from Ti interstitials to the adsorbates.

Given the possibility of electron donation arising from Ti interstitial defects, we studied the interaction of  $O_2$  with the clean  $r$ - $TiO_2(110)$  surface at RT in further detail (Fig. 3). Specifically, we identified a non-vacancy-related  $O_2$  dissociation channel occurring within the Ti troughs. That such a second  $O_2$  dissociation channel exists, in addition to the known dissociation channel associated with  $O_{br}$  vacancies (3, 14, 16, 29, 30), is evident from the high number of paired  $O_{ot}$  adatoms observed on a partially oxidized  $r$ - $TiO_2(110)$  surface (Fig. 3, A and B). After  $O_2$  exposure, the densities of  $O_{br}$  vacancies {3.9% monolayers [MLs; 1 ML is the density of the  $(1 \times 1)$  units,  $5.2 \times 10^{14} \text{ cm}^{-2}$ ]} and  $O_{ot}$  adatoms (6.0% MLs) together exceed the density of  $O_{br}$  vacancies before the exposure (7.9% MLs) by roughly the density of  $O_{ot}$  adatoms found in pairs (1.7% MLs). In the pairs, two  $O_{ot}$  adatoms are adsorbed on next-nearest Ti-5f atoms. Such  $O_{ot}$  pairs were also observed after oxidation of a  $r$ - $TiO_2(110)$  surface with a very low density of  $O_{br}$  vacancies (Fig. 3C), where an unlikely but, in principle, possible  $O_{ot}$  pair formation through two separate  $O_2$  dissociation reactions in  $O_{br}$  vacancies on adjacent  $O_{br}$  rows can be ruled out with certainty.  $O_{ot}$  pairs are

also evident in the STM images reported by Henderson *et al.* (25).

To study the non-vacancy-related  $O_2$  dissociation channel more in depth, we also exposed  $r$ - $TiO_2(110)$  surfaces to  $O_2$  at low temperatures (120 K) and subsequently annealed the crystals to temperatures of 393 K and 448 K, respectively (Fig. 4, A to E). After exposing the surface of a  $TiO_2(110)$  crystal with an  $O_{br}$  vacancy density of 4.5% MLs to 5 L of  $O_2$  at 120 K, all the  $O_{br}$  vacancies disappeared and  $O_{ot}$  adatoms appeared in the Ti troughs (Fig. 4A). No  $O_{ot}$  pairs were evident in the STM images, indicating that the non-vacancy-related  $O_2$  dissociation channel does not operate at this low temperature. This conclusion is consistent with the 1:1 correlation between the density of  $O_{br}$  vacancies before  $O_2$  exposure and the density of  $O_{ot}$  adatoms after the exposure. However, after annealing this  $O_2$ -exposed  $TiO_2(110)$  surface to 393 K (Fig. 4B), the density of  $O_{ot}$  adatoms increased by a factor of  $\sim 2$ . This result shows that the non-vacancy-related  $O_2$  dissociation channel is energetically more activated than the one associated with the  $O_{br}$  vacancies.

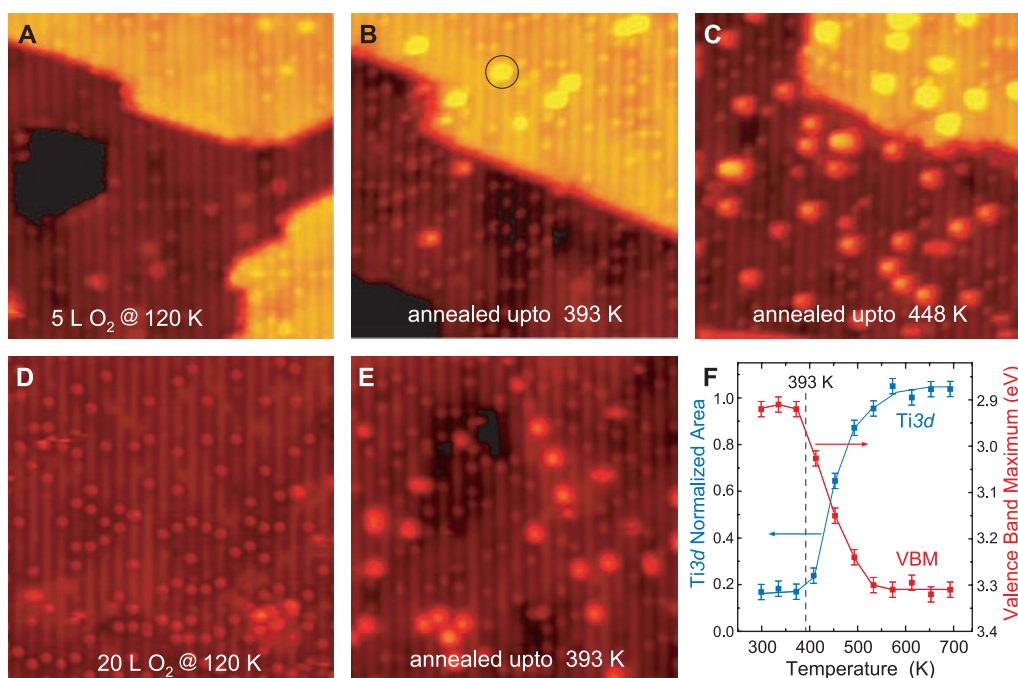
In addition, a number of small islands appeared on the terraces, one of which is indicated in Fig. 4B by a circle. These newly formed islands are positioned in between two Ti troughs and show up in the STM images with a height of  $\sim 2.2 \text{ \AA}$ . Subsequent annealing to an even higher temperature (448 K) led to an increase in the density of the islands, and, in this case, larger islands with a height of  $\sim 3.2 \text{ \AA}$  were observed, in addition to the small islands (Fig. 4C). A height

of  $\sim 3.2 \text{ \AA}$  closely resembles the step height on  $TiO_2(110)$  crystals; that is, the height of one  $TiO_2$  trilayer, which is  $\sim 3.25 \text{ \AA}$ . When applying identical experimental procedures for a more reduced  $TiO_2(110)$  crystal (with an  $O_{br}$  vacancy density of  $\sim 10.8\%$  MLs and  $\sim 9.4\%$  MLs  $O_{ot}$  adatoms density after saturation with 20 L  $O_2$  at 120 K), the density of  $O_{ot}$  adatoms was slightly smaller after annealing to 393 K than before the anneal (Fig. 4, D and E), but, compared with the situation on the low-reduced  $TiO_2(110)$  crystal (Fig. 4B), the number of small islands after annealing to 393 K was higher.

In Fig. 4F, we present PES results for a similar annealing experiment. The  $Ti3d$  defect state reappeared after annealing to temperatures higher than 400 K. In Fig. 4F, the oxidation before the annealing at 400 K was carried out at RT, but we found results when the oxidation was performed at 120 K that were similar to those of the STM experiments depicted in Figs. 4, A to E. Concomitant with the recovery of the  $Ti3d$  defect state, the valence-band maximum (VBM) shifts back to the original value of the clean  $r$ - $TiO_2(110)$  surface.

Based on the STM results (Fig. 4, A to E) and the PES data (Fig. 4F and figs. S2 and S3) (26), we propose the following model. Because exclusively Ti and O features are evident in the PES core-level spectra (fig. S2), the islands appearing on previously flat terraces must be newly formed  $TiO_x$  structures, with  $x \sim 2$ . This finding implies that Ti atoms have diffused from the near-surface region to the topmost surface layer, where reactions with  $O_{ot}$  adatoms and possibly also

**Fig. 4.** (A to C) STM images (150 by 150  $\text{\AA}$ ) of a  $TiO_2(110)$  crystal characterized by an  $O_{br}$ -vacancy density of  $\sim 4.5\%$  MLs, (A) exposed to 5-L  $O_2$  at 120 K, (B) subsequently annealed up to 393 K, and (C) further annealed up to 448 K. The circle in (B) indicates one of the newly formed  $TiO_x$  islands on the terraces with an STM height of  $\sim 2.2 \text{ \AA}$ . (D and E) STM images (150 by 150  $\text{\AA}$ ) of a  $TiO_2(110)$  crystal characterized by an  $O_{br}$ -vacancy density of  $\sim 10.8\%$  MLs, (D) exposed to 20-L  $O_2$  at 120 K leading to an  $O_{ot}$  adatoms density of  $\sim 9.3\%$  MLs and  $\sim 1.8\%$  MLs residual  $O_{br}$  vacancies, and (E) after subsequent annealing up to 393 K where  $TiO_x$  islands have been formed. All STM images were acquired at temperatures between 110 and 130 K. Corresponding PES core-level scans are plotted in fig. S2 (26). Exclusively Ti- and O-related features were found in the PES spectra both after  $O_2$  exposure at 120 K as well as after annealing to temperatures of  $\geq 400$  K. (F) Normalized integrated intensities of the  $Ti3d$  features (left axis, blue) and position of the VBM (right axis, red) as a function of the maximum annealing temperature. The VBM values are given in BE. The underlying valence-band



spectra (fig. S3) were of an  $r$ - $TiO_2(110)$  crystal that was reduced comparably to those crystals that were used to collect the data shown in Fig. 1 and Fig. 4, D and E. The crystal was oxidized at RT by exposing it to 1000 L of  $O_2$ .

with  $O_2$  molecules occurred. The fact that the  $Ti3d$  defect state reappears after annealing to temperatures higher than 400 K can be explained by the migration of Ti interstitials from deeper layers to interstitial sites in the layers nearer the surface that had been depleted in the course of  $TiO_x$  island formation. Assuming a 1:2 correlation between Ti and O in the islands, we estimated a lower limit of Ti interstitials in the near-surface region, corresponding to 5 to 6% MLs for the  $TiO_2(110)$  crystals used in the experiments summarized in Fig. 4.

The STM and PES results shown in Fig. 4 are consistent with the temperature-programmed static secondary ion mass spectrometry data reported by Henderson (19), in which the onset of Ti interstitial diffusion occurred at  $\sim 400$  K. Furthermore, similarities exist to previous STM results by Onishi *et al.* (22) and by Li *et al.* (23), in which  $O_2$ -induced growth of new structures on originally flat  $TiO_2(110)$  terraces were also obtained. However, because the experimental procedures applied in these previous studies were different from the ones in the present work, the structures obtained by Onishi *et al.* (22) and by Li *et al.* (23) are different from the ones obtained here.

The above-presented results addressing the  $O_2$  interaction with  $r$ - $TiO_2(110)$  reveal that Ti charge donors exist in the near-surface region of vacuum-annealed  $TiO_2$  crystals, and that these donor sites strongly influence the  $O_2$  interaction with  $r$ - $TiO_2(110)$ , even at temperatures as low as 120 K. Because the gap state remains largely unaffected by the removal of all surface defects ( $O_{br}$  and  $OH_{br}$ ), we propose that the appearance of the gap state on clean reduced  $TiO_2(110)$  crystals, as is typically observed after vacuum annealing, is mainly associated with the Ti interstitials. Quenching of the gap state and so-called band-bending effects (Figs. 1D and 4F) can be ascribed to the withdrawal of electronic charge from the donor sites in the near-surface region through the accumulation of electronegative adsorbates, such as  $O_2$  and  $O_{ot}$  adatoms on the surface.

To further explore this new interpretation, we performed first-principles DFT calculations using the DACAPO software package (<https://wiki.fysik.dtu.dk/dacapo>), using ultrasoft pseudopotentials and the revised Perdew-Burke-Ernzerhof exchange-correlation functional (26). We assumed a Ti interstitial (Fig. 5, blue) initially between the second and third trilayers of a five- $TiO_2$  trilayer slab with a  $c(4 \times 2)$  surface-unit cell (Fig. 5B). On the surface of such a slab, an adsorbed  $O_2$  molecule binds with  $\sim 1.6$  eV, which is comparable to the  $\sim 1.9$ - and 0.8-to-2.0-eV bond strengths calculated for  $O_2$  on  $r$ - $TiO_2(110)$  (14) and  $h$ - $TiO_2(110)$  (31), respectively. The DFT potential-energy diagram (Fig. 5A) shows that an energetically favorable pathway exists for a Ti interstitial to diffuse to the surface and to react with the adsorbed  $O_2$  molecule to form a  $TiO_2$  island on the terrace. The Ti interstitial diffusion proceeds via an exchange mechanism (21), in which a Ti atom on a regular lattice site (light

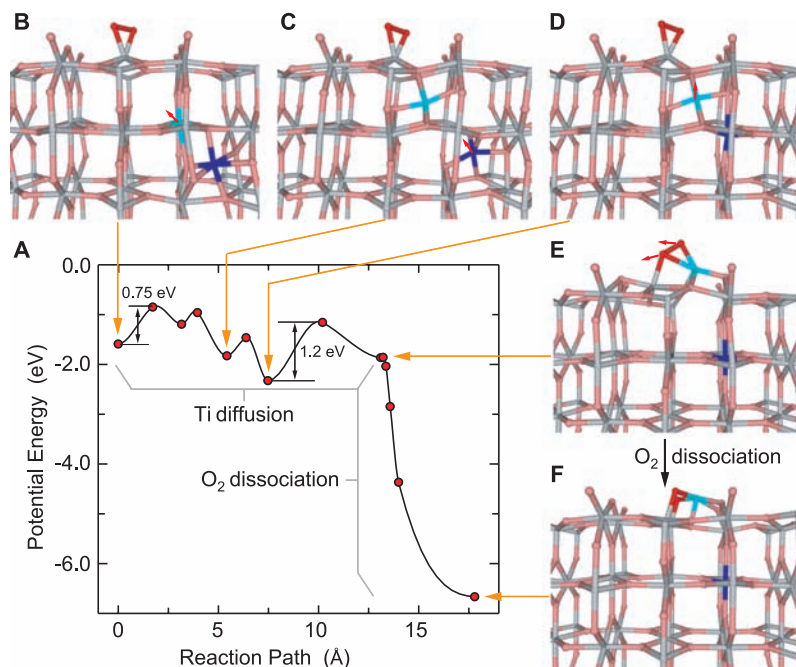
blue) is released to an interstitial site toward the surface (Fig. 5C), and subsequently the lattice site is occupied by the original Ti interstitial atom (dark blue) from a deeper layer (Fig. 5D). Dissociation of the  $O_2$  molecule (Fig. 5, E and F) gains  $\sim 4$  eV in energy.

Relative to the initial configuration (Fig. 5B), the overall barrier for the formation of the  $TiO_x$  islands on the terraces is  $\sim 0.75$  eV. However, with respect to the potential energy of the metastable intermediate configuration of the Ti interstitial between the first and second  $TiO_2$  trilayer (Fig. 5C), the barrier becomes  $\sim 1.2$  eV. The absolute value of this energy barrier is in good agreement with the experimental findings that the  $TiO_x$  islands appear on the flat  $TiO_2(110)$  terraces after annealing to temperatures well above RT (Fig. 4). If we tentatively assume that the Ti diffusion can be described as a first-order process, our rough estimate of the diffusion barrier from the Redhead formula is 1.2 eV.

If we start with a configuration wherein the  $O_2$  molecule in Fig. 5 is replaced by an  $O_{ot}$  adatom, our DFT calculations still indicate favorable energetics for the diffusion of the Ti interstitial toward the surface. The two adsorbates,  $O_2$  and  $O_{ot}$  adatoms, are quite similar electronically. According to a Bader charge analysis of our slab systems (26), a molecularly adsorbed  $O_2$  species withdraws  $\sim 0.9$  electron ( $e$ ) from the  $TiO_2(110)$  substrate, whereas an  $O_{ot}$  adatom

withdraws  $\sim 0.8 e$ . If these electronegative adsorbates are removed from the  $TiO_2(110)$  surface layer, the most favorable position of the Ti interstitial is the octahedral site (32) between the second and third  $TiO_2$  trilayer. For a six- $TiO_2$  trilayer slab, our calculations show that the potential energy is higher by  $\sim 0.40$  and  $\sim 0.23$  eV, respectively, when locating the Ti interstitial one- $TiO_2$  trilayer higher or lower in the [110] direction.

To elucidate the mechanism of the second  $O_2$  dissociation channel identified experimentally in Fig. 3 and Fig. 4, A and B, we performed additional calculations (figs. S4 and S5) (26). In agreement with previous reports (14, 33, 34), we found that  $O_2$  molecules neither adsorb nor dissociate on stoichiometric  $TiO_2(110)$  unless the slab is reduced. Introduction of an  $O_{br}$  vacancy is sufficient to enable the adsorption of molecular  $O_2$  (fig. S4B) (26) but not to dissociate  $O_2$  in the Ti trough (fig. S4C) (26). Instead, when reducing the slab by adding a near-surface Ti interstitial, both the molecular (fig. S4D) and the dissociative adsorption (fig. S4E) of  $O_2$  become feasible. If a Ti interstitial and an  $O_{br}$  vacancy occur simultaneously, the energy gain is even greater in both these adsorption modes (fig. S4, F and G). The experimental observation in Fig. 3 and Fig. 4, A and B, that dissociation of  $O_2$  in the Ti troughs leads to next-nearest neighbors of  $O_{ot}$  adatoms is supported by the calculated preference for this configuration (fig. S5D) as com-



**Fig. 5.** (A) Potential-energy profile for the reaction of an adsorbed  $O_2$  molecule and a Ti interstitial on  $TiO_2(110)$ . The energy zero corresponds to  $O_2$  in the gas phase and the Ti interstitial at the octahedral position between the second and third  $TiO_2$  trilayer. (B) Adsorbed  $O_2$  molecule (red). (C) Ti interstitial (dark blue) moved to tetrahedral position and lattice Ti (light blue) to tetrahedral position between the first and the second  $TiO_2$  trilayer. (D) Original Ti interstitial (dark blue) now at lattice position. (E) Exchanged Ti interstitial (light blue) appearing at the surface. (F) Adsorbed  $O_2$  dissociated and a surface  $TiO_2$  island formed at the terrace. Orange arrows indicate positions on the potential-energy profile that correspond to the configurations shown in (B) to (F).



pared with a pair of nearest-neighbor  $O_{ot}$  adatoms (fig. S5C).

The role of the Ti interstitials in the  $O_2$  adsorption and dissociation reactions is to provide the electronic charge for the adsorbates. According to the above Bader charge analysis, more electronic charge is required for dissociative adsorption ( $2O_{ot}$ ) than for molecular adsorption ( $1O_2$ ). Hence, dissociative adsorption is more sensitive to the amount of charge available on the surface than molecular adsorption, a fact clearly borne out by the DFT calculations in figs. S4 and S5. For instance, coadsorption of  $O_{ot}$  in fig. S5, B to D, decreases the stability of molecularly adsorbed  $O_2$  by  $\sim 0.4$  eV (fig. S5, B versus E) but that of dissociatively adsorbed oxygen by  $\sim 1.5$  eV (fig. S5, C and D versus F and G). The coadsorbed  $O_{ot}$  adatom partially oxidizes the surface and thereby lowers the ease with which electronic charge is available for further surface reactions.

Within the scheme used for the calculations, the  $O_2$  dissociation energy barrier is increased from  $\sim 0.3$  to  $\sim 0.8$  eV (fig. S5A) upon introduction of the  $O_{ot}$  adatom. This result explains why the coverage of  $O_{ot}$  adatoms remains low even under conditions in which the second  $O_2$  dissociation channel operates (Fig. 3C); that is, the reaction is self-limiting. Similarly, some  $O_{br}$  vacancies remain unfilled even in the case of  $O_2$  saturation (Figs. 1C and 4D); that is, the electronic charge required for the resulting  $O_{ot}$  adatoms depletes the source from the limited number of Ti interstitials. This charge-competition model also could explain why an  $O_2$  desorption feature observed in the temperature-programmed desorption experiments by Henderson *et al.* (30) is evident only after exposing the *r*- $TiO_2(110)$  surface at low temperature (below  $\sim 180$  K). If impinging  $O_2$  molecules can overcome the dissociation barrier, as observed in the experiments performed at RT (Fig. 3), the dissociation products deplete the electron donors in the bulk, and the accumulation of molecular  $O_2$  is prohibited.

For a slab characterized by a Ti interstitial between the second and third  $TiO_2$  trilayer and a pristine surface, our calculations reveal the existence of a gap state. This state lies  $\sim 2$  eV above the VBM, in good agreement with the state observed in the PES experiments (Figs. 1D and 2E) as well as with DFT calculations addressing Ti interstitials in the bulk (32). A thorough analysis (fig. S6, A and B) of the spatially resolved electronic density of states shows that the gap state is spatially located in the region between the second and third  $TiO_2$  trilayer, which strongly suggests that its origin is from the Ti interstitial. Further reduction of the surface layer by introduction of an  $O_{br}$  vacancy or a capping H atom ( $OH_{br}$  group) does not affect the gap state (fig. S6, C and D).

Conversely, adsorption of electronegative species such as  $O_2$  or  $O_{ot}$  adatoms causes quenching of the gap state (fig. S6, E and F); in the case of adsorbed  $O_2$ , a new  $O_2$ -related state appears in the gap, in agreement with electron energy loss

results by Henderson *et al.* (30). Most previous DFT papers addressing the gap state did not reveal a state in the gap for stoichiometric  $TiO_2$  slabs with  $O_{br}$  vacancies or  $OH_{br}$  groups (11). Our calculations agree with these previous results (fig. S7, A to C) and further show no sign of a gap state when we introduce a hypothetical O vacancy in the bulk (fig. S7, D and E). These results challenge the conclusions derived by Di Valentin *et al.* (10) that a hybrid DFT setup is required to identify the gap state and that the gap state is related to  $O_{br}$  vacancies.

We propose that the surface redox chemistry on reduced titania is to a large extent associated with Ti interstitials in the near-surface region, because these defect sites provide the electronic charge, enabling important reactions. This conclusion is consistent with numerous experimental studies addressing the  $Ti3d$  defect state, including the pioneering work by Henrich *et al.* (5, 8), electron paramagnetic resonance spectroscopy (35–37), bulk photonic (38) and transport (39) studies, recent photoelectron diffraction studies (40), and thin-film growth studies (41).

Moreover, several experimental results that were puzzling within an O vacancy model can now be revisited and explained more readily. For example, the simultaneous UPS and metastable impact electron spectroscopy (MIES) measurements of *r*- $TiO_2(110)$  by Krischok *et al.* show no intensity between 0.5 to 1.0 eV below  $E_F$  in the MIES spectrum, whereas the  $Ti3d$  defect state is clearly observed in the UPS spectrum (13). Because of enhanced surface sensitivity with MIES as compared with UPS, the intensity of the  $Ti3d$  defect state is strongly suppressed in MIES (13). As a second example, it can be rationalized why the  $Ti3d$  defect state occurs for reduced bulk  $TiO_2$  single crystals, but not for titania thin films grown on metal substrates. Particularly in the case of ultrathin titania films (4, 42), there are no interstitial sites available and, hence, a defect state typical of reduced  $TiO_2$  single crystals does not occur (4, 42). Instead, the *d* electrons of the metal substrate can be considered a huge “bulk defect state” and thus fulfill the same function that the Ti interstitials do in reduced bulk  $TiO_2$  crystals. Finally, at interfaces between two isolating oxide materials, the Ti interstitials may be the cornerstone to explain phenomena such as superconductivity, as has been reported for  $LaAlO_3/SrTiO_3$  (43).

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#### Supporting Online Material

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