The Role of Interstitial Sites in the Ti*3d* Defect State in the Band Gap of Titania

Stefan Wendt,[1] Phillip T. Sprunger,[1,2] Estephania Lira,[1] Georg K. H. Madsen,[1] Zheshen Li,[1] Jonas Ø. Hansen,[1] Jesper Matthiesen,[1] Asger Blekinge-Rasmussen,[1] Erik Lægsgaard,[1] Bjørk Hammer,[1*] Flemming Besenbacher[1*]

[1]Interdisciplinary Nanoscience Center (iNANO), Department of Physics and Astronomy, and Institute for Storage Ring Facilities (ISA), University of Aarhus, DK-8000 Aarhus C, Denmark. [2]Department of Physics and Astronomy, Louisiana State University, Baton Rouge, LA 70808, USA.

*To whom correspondence should be addressed. E-mail: hammer@phys.au.dk (B.H.); fbe@inano.dk (F.B.)

Titanium dioxide has a number of uses in catalysis, photochemistry and sensing that are linked to the reducibility of the oxide. Usually, bridging oxygen (O_{br}) vacancies are assumed to cause the Ti*3d* defect state in the band gap of rutile TiO_2(110). From high-resolution scanning tunneling microscopy and photo-electron spectroscopy measurements we here 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 significant role in and may dictate the ensuing surface chemistry, such as providing the electronic charge required for O_2 adsorption and dissociation. Specifically, we identified a second O_2 dissociation channel that occurs within the Ti troughs in addition to the O_2 dissociation channel in O_{br} vacancies. Comprehensive density functional theory calculations support these experimental observations.

Titania (TiO_2) 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; but its applications are enabled by excess electrons originating from the defect state that is located within the band gap of reduced titania (TiO_{2-x}). 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 Ti*3d* derived state in the band gap (*5–7*) at ~0.85 eV below the Fermi level (E_F) has been fully ascribed to O_{br} vacancies, because, in an ionic picture, the two excess electrons per O_{br} 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_2(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_2 exposure (*8, 12, 13*). Seemingly further support for the O vacancy model came from scanning tunneling microscopy (STM) (*14–17*) and atomic force microscopy (*18*) studies, where O_{br} vacancies have been clearly identified on TiO_2(110). Although most first-principles 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_2(110) crystals has been noted. For example, the re-oxidation of sputtered TiO_2(110) surfaces via vacuum annealing has been explained via Ti interstitial diffusion into the bulk (*19–21*). Similarly, when a reduced TiO_2(110) crystal is exposed to O_2 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 on titania.

By means of high-resolution STM and photoelectron spectroscopy (PES) measurements in conjunction with density functional theory (DFT) calculations, we have systematically explored the origin of the Ti*3d* defect state in the band gap. We found that the gap state remains almost unchanged on surfaces where the O_{br} 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_2 dissociation channel in O_{br} vacancies, we discovered a non-vacancy related O_2 dissociation channel that occurs within the Ti troughs.

The TiO$_2$(110)–(1 × 1) surface consists of alternating rows of fivefold-coordinated Ti (5f-Ti) atoms (the Ti troughs) and protruding, twofold coordinated O$_{br}$ atoms. As bulk Ti atoms in stoichiometric rutile, the Ti atoms underneath the O$_{br}$ atoms are six-fold coordinated. Ion sputtering and vacuum-annealing the TiO$_2$(110) crystal results in a reduced n-type semiconductor, with a bulk conductivity that allows for use of STM and other electron spectroscopy techniques. Consistent with previous findings (6), the STM images (Fig. 1) of the TiO$_2$(110) surface are dominated by electronic effects, i.e. the bright rows correspond to the Ti troughs, whereas geometrically protruding O$_{br}$ atoms appear as the dark troughs in the STM images (6).

A high-resolution STM image recorded on a clean reduced TiO$_2$(110) surface [r-TiO$_2$(110)] (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$_2$] 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 OH3σ feature at a binding energy (BE) of ~10.8 eV that is evident in the valence band after hydration (12). Surprisingly, the Ti$3d$ defect state at ~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 a 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 ad-atoms that reside on top of 5f-Ti atoms (O$_{ot}$). However, O$_2$ exposure at RT does not lead to healing of all O$_{br}$ vacancies even in case of saturation (26). In the valence band spectrum corresponding to the O$_2$ exposed TiO$_2$(110) surface, the most striking feature is the strongly suppressed defect state at ~0.85 eV (Fig. 1D). In addition, compared to the spectra for r- and h-TiO$_2$(110), the dominating features between BE's of ~3 and ~9.5 eV [primarily O$2p$ derived (5, 7, 12, 27)] were found to be shifted by ~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 Ti$3d$ 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$_{ot}$ ad-atoms 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 Ti$3d$ 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$_{ot}$ ad-atoms.

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 indeed 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 identical surface preparations as in the STM experiments and focused on the OH3σ feature at ~10.8 eV and on the Ti$3d$ defect state (Fig. 2E). The OH3σ feature was completely attenuated after an O$_2$ exposure of 4 L, whereas much higher exposures were required to minimize the Ti$3d$ defect state (420 L). For clarity, the evolution of the Ti$3d$ defect state and the OH3σ feature are shown in Fig. 2F in greater detail, and the development of the OH3σ feature for O$_2$ exposures ≤4 L is shown in figure S1 (26). The most striking 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 Ti$3d$ 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 Ti$3d$ defect state is neither caused by O$_{br}$ vacancies nor by capping H atoms on the O$_{br}$ rows. Rather, we will show that the Ti$3d$ 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 indeed 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$_{ot}$ ad-atoms observed on a partially oxidized r-TiO$_2$(110) surface (Fig. 3, A and B). After O$_2$

exposure, the density of O_{br} vacancies (3.9% ML) and O_{ot} ad-atoms (6.0% ML) together exceeds the density of O_{br} vacancies prior to the exposure (7.9% ML) by roughly the density of O_{ot} ad-atoms found in pairs (1.7% ML). In the pairs, two O_{ot} ad-atoms are adsorbed on next-nearest Ti-5f atoms. Such O_{ot} pairs were also observed after oxidation of an 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. Interestingly, 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 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%ML to 5 L O_2 at 120 K, all the O_{br} vacancies disappeared and O_{ot} ad-atoms 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 prior to O_2 exposure and the density of O_{ot} ad-atoms after the exposure. However, after annealing of this O_2 exposed TiO$_2$(110) surface to 393 K (Fig. 4B), the density of O_{ot} ad-atoms increased by a factor of ~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 ~2.2 Å. Subsequent annealing to an even higher temperature (448 K) led to an increase in the density of the islands, and, in this case, islands with a height of ~3.2 Å were observed, in addition to the islands of ~2.2 Å height (Fig. 4C). In this context, we note that a height of ~3.2 Å closely resembles the step height on TiO$_2$(110) crystals, i.e. the height of one TiO$_2$ tri-layer which is ~3.25 Å. When applying identical experimental procedures for a more reduced TiO$_2$(110) crystal (O_{br} vacancy density ~10.8%ML and ~9.4%ML O_{ot} ad-atoms density after saturation with 20 L O_2 at 120 K), the density of O_{ot} ad-atoms was slightly smaller after annealing to 393 K than prior to 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 TiO$_x$ islands after annealing to 393 K was higher.

In Fig. 4F we present PES results for a similar annealing experiment. The Ti$3d$ defect state reappeared after annealing to temperatures higher than 400 K. In Fig. 4F, the oxidation

prior to the annealing at 400 K was carried out at RT, but we found similar results when the oxidation was performed at 120 K as for the STM experiments depicted in Figs. 4, A to E. Concomitant with the recovery of the Ti$3d$ 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, fig. 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. This finding implies that Ti atoms have diffused from the near-surface region to the top-most surface layer where reactions with O_{ot} ad-atoms and possibly also with O_2 molecules occurred. That the Ti$3d$ defect state reappears after annealing to temperatures higher than 400 K can be explained by 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 estimate a lower limit of Ti interstitials in the near-surface region corresponding to 5 to 6% ML 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 temperature-programmed static secondary ion mass spectrometry data reported by Henderson (*19*), where the onset of Ti interstitial diffusion occurred at ~400 K. Furthermore, similarities exist to previous STM results by Onishi *et al.* (*22*) and by Li *et al.* (*23*), where 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 compared to the one 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 indeed 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 typically obtained after vacuum-annealing is mainly associated with the Ti interstitials. Quenching of the gap state and so-called band bending effects (Fig. 1D, Fig. 4F) can be ascribed to 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} ad-atoms on the surface.

To further explore this new interpretation, we performed first-principles DFT calculations using the DACAPO

package, employing ultrasoft pseudopotentials and the revised Perdew-Burke-Ernzerhof (RPBE) exchange-correlation functional (*26*). We assumed a Ti interstitial (Fig. 5, blue sphere) initially between the 2nd and 3rd tri-layers of a five TiO_2 tri-layer 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 ~1.6 eV, which is comparable to the ~1.9 and 0.8–2.0 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 TiO_x islands on the terraces. The Ti interstitial diffusion proceeds via an exchange mechanism (*21*), where a Ti atom on a regular lattice site (cyan sphere) is released to an interstitial site toward the surface (Fig. 5C), and subsequently the lattice site is occupied by the original Ti interstitial atom (blue sphere) from a deeper layer (Fig. 5D). Dissociation of the O_2 molecule (Fig. 5, E and F) gains ~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 ~0.75 eV. However, with respect to the potential energy of the meta-stable intermediate configuration of the Ti interstitial between the 1st and 2nd TiO_2 tri-layer (Fig. 5C), the barrier becomes ~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} ad-atom, 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} ad-atoms, are quite similar electronically. According to a Bader charge analysis of our slab systems (*26*), a molecularly adsorbed O_2 species withdraws ~0.9 e$^-$ from the $TiO_2(110)$ substrate, whereas an O_{ot} ad-atom withdraws ~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 2nd and 3rd TiO_2 tri-layer. For a six TiO_2 tri-layer slab, our calculations show that the potential energy is higher by ~0.40 and ~0.23 eV, respectively, when locating the Ti interstitial one TiO_2 tri-layer 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 (fig. S4 and fig. 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 energetics for these two adsorption modes is even more favourable (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} ad-atoms is supported by the calculated preference for this configuration (fig. S5D) compared to a pair of nearest-neighbor O_{ot} ad-atoms (fig. S5C).

The role of the Ti interstitials in the O_2 adsorption and dissociation reaction 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 associative adsorption, a fact clearly borne out by the DFT calculations in fig. S4 and fig. S5. For instance, coadsorption of O_{ot} in fig S5, B to D, decreases the stability of molecularly adsorbed O_2 by ~0.4 eV (Fig. S5, B vs. E) but that of dissociatively adsorbed oxygen by ~1.5 eV (fig. S5, C and D versus F and G). The coadsorbed O_{ot} ad-atom 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 ~0.3 to ~0.8 eV (fig. S5A) upon introduction of the O_{ot} ad-atom. This result explains why the coverage of O_{ot} ad-atoms remains low even under conditions where 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 case of O_2 saturation (Fig. 1C and Fig. 4D), that is, the electronic charge required for the resulting O_{ot} ad-atoms 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 temperature programmed desorption experiments by Henderson *et al*. (*30*) is evident only after exposing the r-$TiO_2(110)$ surface at low temperature (below ~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.

Interestingly, for a slab characterized by a Ti interstitial between the second and third TiO_2 tri-layer and a pristine surface, our calculations reveal the existence of a gap state. This state lies ~2 eV above the valence band maximum, in good agreement with the state observed in the PES

experiments (Fig. 1D and Fig. 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, sDOS, shows that the gap state is spatially located in the region between the second and third TiO_2 tri-layer, which strongly suggests 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 electro-negative species such as O_2 or O_{ot} ad-atoms causes quenching of the gap state (fig. S6, E and F); in case of adsorbed O_2 a new O_2 related state appears in the gap, in agreement with electron energy loss (ELS) results by Henderson *et al.* (*30*). We note that the major part of 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 Ti*3d* defect state, including the pioneering work by Henrich *et al.* (*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 on *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 Ti*3d* defect state is clearly observed in the UPS spectrum (*13*). Because of enhanced surface sensitivity with MIES compared to UPS, the intensity of the Ti*3d* defect state is strongly suppressed in MIES (*13*). As a second example, it can be rationalized why the Ti*3d* 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 as a huge "bulk defect state" and thus fulfill the same function as the Ti interstitials do in reduced bulk TiO_2 crystals. Finally,

we note that at interfaces between two isolating oxide materials the Ti interstitials maybe the corner stone to explain such exiting phenomena like superconductivity as reported for $LaAlO_3$/$SrTiO_3$ (*43*).

References and Notes

1. M. Haruta, T. Kobayashi, H. Sano, N. Yamada, *Chem. Lett.*, 405 (1987).
2. M. Valden, X. Lai, D. W. Goodman, *Science* **281**, 1647 (1998).
3. D. Matthey *et al.*, *Science* **315**, 1692 (2007).
4. M. Chen, Y. Cai, Z. Yan, D. W. Goodman, *J. Am. Chem. Soc.* **128**, 6341 (2006).
5. V. E. Henrich, P. Cox, *The Surface Science of Metal Oxides* (Cambridge Univ. Press, Cambridge, 1996).
6. U. Diebold, *Surf. Sci. Rep.* **48**, 53 (2003).
7. A. G. Thomas *et al.*, *Phys. Rev. B* **75**, 035105 (2007).
8. V. E. Henrich, G. Dresselhaus, H. J. Zeiger, *Phys. Rev. Lett.* **36**, 1335 (1976).
9. T. L. Thompson, J. T. Yates, *Chem. Rev.* **106**, 4428 (2006).
10. C. Di Valentin, G. Pacchioni, A. Selloni, *Phys. Rev. Lett.* **97**, 166803 (2006).
11. M. V. Ganduglia-Pirovano, A. Hofmann, J. Sauer, *Surf. Sci. Rep.* **62**, 219 (2007).
12. R. L. Kurtz, R. Stockbauer, T. E. Madey, E. Roman, J. L. Desegovia, *Surf. Sci.* **218**, 178 (1989).
13. S. Krischok, J. Günster, D. W. Goodman, O. Höfft, V. Kempter, *Surf. Interface Anal.* **37**, 77 (2005).
14. S. Wendt *et al.*, *Surf. Sci.* **598**, 226 (2005).
15. S. Wendt *et al.*, *Phys. Rev. Lett.* **96**, 066107 (2006).
16. O. Bikondoa *et al.*, *Nat. Mater.* **5**, 189 (2006).
17. Z. Zhang, O. Bondarchuk, B. D. Kay, J. M. White, Z. Dohnálek, *J. Phys. Chem. B* **110**, 21840 (2006).
18. J. V. Lauritsen *et al.*, *Nanotechnology* **17**, 3436 (2006).
19. M. A. Henderson, *Surf. Sci.* **419**, 174 (1999).
20. K. T. Park, M. Pan, V. Meunier, E. W. Plummer, *Phys. Rev. B* **75**, 245415 (2007).
21. H. Iddir, S. Ogut, P. Zapol, N. D. Browning, *Phys. Rev. B* **75**, 073203 (2007).
22. H. Onishi, Y. Iwasawa, *Phys. Rev. Lett.* **76**, 791 (1996).
23. M. Li *et al.*, *Surf. Sci.* **437**, 173 (1999).
24. R. A. Bennett, P. Stone, N. J. Price, M. Bowker, *Phys. Rev. Lett.* **82**, 3831 (1999).
25. M. A. Henderson, J. M. White, H. Uetsuka, H. Onishi, *J. Am. Chem. Soc.* **125**, 14974 (2003).
26. Materials and methods are available as supporting material on *Science* Online.
27. J. C. Woicik *et al.*, *Phys. Rev. Lett.* **89**, 077401 (2002).
28. M. A. Henderson, W. S. Epling, C. H. F. Peden, C. L. Perkins, *J. Phys. Chem. B* **107**, 534 (2003).
29. W. S. Epling, C. H. F. Peden, M. A. Henderson, U. Diebold, *Surf. Sci.* **413**, 333 (1998).

30. M. A. Henderson, W. S. Epling, C. L. Perkins, C. H. F. Peden, U. Diebold, *J. Phys. Chem. B* **103**, 5328 (1999).
31. L. M. Liu, B. McAllister, H. Q. Ye, P. Hu, *J. Am. Chem. Soc.* **128**, 4017 (2006).
32. E. Cho *et al.*, *Phys. Rev. B* **73**, 193202 (2006).
33. M. D. Rasmussen, L. M. Molina, B. Hammer, *J. Chem. Phys.* **120**, 988 (2004).
34. Z. Dohnálek, J. Kim, O. Bondarchuk, J. M. White, B. D. Kay, *J. Phys. Chem. B* **110**, 6229 (2006).
35. M. Li *et al.*, *J. Phys. Chem. B* **104**, 4944 (2000).
36. A. L. Attwood, D. M. Murphy, J. L. Edwards, T. A. Egerton, R. W. Harrison, *Res. Chem. Intermediat.* **29**, 449 (2003).
37. M. Aono, R. R. Hasiguti, *Phys. Rev. B* **48**, 12406 (1993).
38. A. K. Ghosh, F. G. Wakim, R. R. Addiss, *Phys. Rev.* **184**, 979 (1969).
39. E. Yagi, R. R. Hasiguti, M. Aono, *Phys. Rev. B* **54**, 7945 (1996).
40. P. Krüger *et al.*, *Phys. Rev. Lett.* **100**, 055501 (2008).
41. S. A. Chambers *et al.*, *Chem. Phys.* **339**, 27 (2007).
42. P. Finetti *et al.*, *J. Phys. Chem. C* **111**, 869 (2007).
43. N. Reyren *et al.*, *Science* **317**, 1196 (2007).
44. We acknowledge financial support from the Danish Ministry of Science, Technology, and Innovation through iNANO, the Danish Research Councils, and the Danish Center for Scientific Computing. P.T.S. acknowledges support through NSF DMR/0504654 and -/CHE-0615606.

Supporting Online Material

Fig. 1. STM images (105 Å by 105 Å) of *r*-TiO$_2$(110) (**A**), *h*-TiO$_2$(110) (**B**), and an at RT O$_2$ saturated TiO$_2$(110) surface acquired with a sample in a reduction state corresponding to an O$_{br}$ vacancy density of $11.4 \pm 0.3\%$ ML, where one ML (monolayer) is defined as the density of the (1×1) units, 5.2×10^{14} / cm^2. Symbols indicate O$_{br}$ vacancies (square), capping H atoms (hexagon) in the O$_{br}$ rows, and O$_{ot}$ ad-atoms (circle) as well as pairs of next-nearest O$_{ot}$ ad-atoms (ellipse) in the Ti troughs. STM images were collected with a tunneling current (I_t) ≤ 0.1 nA and a tunneling voltage (V_t) = 1.2 V. Directions are identical throughout the paper as 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 the label "VBM" and the Ti$3d$ defect state is observed within the ~ 3.1 eV wide band gap.

Fig. 2. (**A** to **D**) STM images (105 Å by 105 Å) acquired on 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 $5.5 \pm 0.2\%$ ML. (**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 $11.4 \pm 0.3\%$ ML. (**F**) Normalized, integrated intensities of the OH3σ (red) and Ti$3d$ (blue) features for O$_2$ exposures up to 420 L from PES spectra; circles are used to 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 Å by 155 Å) acquired after 2 L O$_2$ exposure. White crosses indicate pairs of next-nearest O$_{ot}$ ad-atoms. (**B**) Zoom-in STM image (38 Å by 38 Å) in the area as indicated in (A). White squares indicate O$_{br}$ vacancies. (**C**) Zoom-in STM image (38 Å by 38 Å) acquired after 200 L O$_2$ exposure at RT. Prior to O$_2$ exposure this *r*-TiO$_2$(110) crystal was characterized by an O$_{br}$ vacancy density of only ~1.7%ML. STM images were acquired at temperatures between 110 and 130 K.

Fig. 4. (**A** to **C**) STM images (150 Å by 150 Å) acquired on a TiO$_2$(110) crystal characterized by an O$_{br}$ vacancy density of ~4.5%ML. (A) exposed to 5 L O$_2$ at 120 K, (B) subsequently annealed upto 393 K, and (C) further annealed upto 448 K. A circle in (B) indicates one of the newly formed TiO$_x$ islands on the terraces with an STM height of ~2.2 Å. (**D** and **E**) STM images (150 Å by 150 Å) acquired on a TiO$_2$(110) crystal characterized by an O$_{br}$ vacancy density of ~10.8%ML. (D) exposed to 20 L O$_2$ at 120 K leading to an O$_{ot}$ ad-atoms density of ~9.3%ML and ~1.8%ML residual O$_{br}$ vacancies, and (E) after subsequent annealing upto 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 ≥ 400 K. (**F**) Normalized, integrated intensities of the Ti$3d$ features (left axis, blue color) and position of the valence band maximum (right axis, red color) as a function of the maximum annealing temperature. The valence band maximum (VBM) values are given in terms of binding energy. The underlying valence band spectra (Fig. S3) were acquired on an *r*-TiO$_2$(110) crystal which was comparably reduced as those crystals 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$_2$.

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 tri-layer. (**B**) Adsorbed O_2 molecule. (**C**) Ti interstitial (blue sphere) moved to tetrahedral position and lattice Ti (cyan sphere) to tetrahedral position between the first and the second TiO_2 tri-layer. (**D**) Original Ti interstitial (blue sphere) now at lattice position. (**E**) Exchanged Ti interstitial (cyan sphere) appearing at the surface. (**F**) Adsorbed O_2 dissociated and a surface TiO_2 island formed at the terrace.

A

+ H₂O →

r-TiO₂

+ O₂ @ RT ↓

C

○ ⬭

[001]
[1̄10]

B

h-TiO₂

+ O₂ @ RT ↓

see Fig. 2

D

hν = 47.5 eV

OH3σ   Ti3d

VBM   E_F

r-TiO₂

h-TiO₂   0.4 eV

1000 L
O₂ @ RT

Intensity (arb. units)

Binding Energy (eV)

A h-TiO₂

E hν = 47.5 eV

OH3σ   Ti3d   E_F

O₂ exposure

4 L

40 L

420 L

Binding Energy (eV)

Intensity (arb. units)

F h-TiO₂(110): oxygen exposure at room temperature

Normalized Area

OH3σ

Ti3d

O₂ Exposure (L)

A — r-TiO$_2$ + 2 L O$_2$ @ RT

B — paired O$_{ot}$

C — paired O$_{ot}$

A 5 L O$_2$ @ 120 K

B annealed upto 393 K

C annealed upto 448 K

D 20 L O$_2$ @ 120 K

E annealed upto 393 K

F

393 K

Ti3d

VBM

Ti3d Normalized Area

Valence Band Maximum (eV)

Temperature (K)

B

C

D

A

0.75 eV

Ti diffusion

O_2 dissociation

1.2 eV

Potential Energy (eV)

Reaction Path (Å)

E

O_2 dissociation

F