Observation and Destruction of an Elusive Adsorbate with STM: $O_2/TiO_2(110)$

Philipp Scheiber, Alexander Riss,[*] Michael Schmid, Peter Varga, and Ulrike Diebold[†]

Institute of Applied Physics, Vienna University of Technology,
Wiedner Hauptstrasse 8-10, 1040 Vienna, Austria

When a slightly defective rutile $TiO_2(110)$ surface is exposed to O_2 at elevated temperatures, the molecule dissociates at defects, filling O vacancies (V_O) and creating O adatoms (O_{ad}) on Ti_{5c} rows. The adsorption of molecular O_2 at low temperatures has remained controversial. Low-temperature scanning tunneling microscopy of O_2, dosed on $TiO_2(110)$ at a sample temperature of ≈ 100 K and imaged at 17 K, shows a molecular precursor at V_O as a faint change in contrast. The adsorbed O_2 easily dissociates during the STM measurements, and the formation of O_{ad}'s at both sides of the original V_O is observed.

The adsorption of oxygen on TiO_2 is a fascinating topic from both an applied and a fundamental point of view. Adsorbed oxygen plays a key role in photocatalysis, both as an electron scavenger and as the oxidative species. It is important in low-temperature oxidation processes in heterogeneous catalysis, and its effect on conductivity is central to semiconductor-based gas sensing. Thus, much effort has been devoted to understanding this interaction in detail [1–20], by using the rutile $TiO_2(110)$ surface [21,22] as a model system. On a stoichiometric $TiO_2(110)$ surface, O_2 only physisorbs and desorbs below ≈ 75 K [15]. This is in agreement with density functional theory-based calculations that predict that excess charge, i.e., O-deficient TiO_2, is essential for chemisorption [12,16,23]. A slightly reduced TiO_2 sample exhibits two main kinds of defects in the near-surface region: O vacancies (V_O) at twofold coordinated, "bridging" atoms (O_{br}) and subsurface Ti interstitials (Ti_{int}). How oxygen adsorbs at room temperature is well understood [1,2,16]: The molecule dissociates at a V_O, filling the vacancy and resulting in an O adatom (O_{ad}) that is singly coordinated to a fivefold coordinated Ti surface atom (Ti_{5c}). Recently, it has been pointed out that O_2 can also dissociate at subsurface Ti_{int}'s, which results in two O_{ad}'s located closely to each other at the same Ti_{5c} row [2]. Oxygen exposure at slightly elevated temperature, where the Ti_{int}'s are more mobile and can migrate to the surface, results in regrowth of excess TiO_x in various configurations [18–20]. STM has been very helpful in unraveling these details of the interaction between O_2 and defects on TiO_2.

What happens at low temperature is less clear, however. When O_2 is dosed on a cold sample, typically at a temperature around 100 K, various desorption techniques—thermal desorption as well as stimulated desorption by electrons or photons—consistently show the formation of a chemisorbed, molecular precursor [3–7]. The O_2 molecule is negatively charged, likely resembling a peroxide O_2^{2-} or superoxide O_2^- ion, and stimulated desorption of this species is hole-mediated [6–9]. One interesting and somewhat mysterious aspect of these experiments is the fact that some of this molecular O_2 desorbs at temperatures well above room temperature: ≈ 400 K [3,4]. Based on thermal desorption and stimulated desorption by electrons measurements, Kimmel and Petrik [3] postulated the formation of a stable O_4^{2-} species ("tetraoxygen") that survives up to these high temperatures without dissociating. To test this prediction and clarify the situation, STM measurements could be quite useful. So far, however, molecular oxygen on TiO_2 was never directly observed with STM.

Here we report low-temperature (17 K) STM results of slightly reduced $TiO_2(110)$ surfaces exposed to O_2 at 100 K. We provide evidence that O_2 is indeed located at V_O's and that it is visible in STM as a rather faint change of the contrast. The O_2 molecule is dissociated by the STM during the measurements even at the smallest tunneling currents applied (4 pA). We were also able to observe the intermediates of O_2 dissociation on $TiO_2(110)$.

The experiments were performed on two different rutile $TiO_2(110)$ crystals, one from CrysTec and the other one from MTI Corp. Both were cleaned by repeated cycles of sputtering (2 keV Ar^+, fluence of 4×10^{16} Ar^+ ions per cm^2) and annealing (at 1123 and 923 K, respectively), resulting in a surface V_O concentration of ≈ 0.17 ML. Constant current STM measurements have been performed in a two-chamber Omicron UHV system with a base pressure below 2×10^{-11} mbar, at sample temperatures of 17 (liquid He cooled) or 78 K (liquid nitrogen cooled). Temperatures of less than 17 K resulted in unstable tunneling. Positive sample bias voltages between 1.3 and 2.4 V were used, and tunneling currents were varied between 0.004 and 0.4 nA. Oxygen dosing was done by backfilling the preparation chamber with a pressure of 1×10^{-9} mbar.

A series of STM images after dosing 0.045 Langmuirs (L; 1 L $= 10^{-6}$ torr s) O_2 at 100 K is shown in Fig. 1. It is well established that the bright and dark lines in empty-state STM images correspond to the rows of Ti_{5c} and bridging oxygen (O_{br}) atoms, respectively [24], and that V_O's appear as short bright lines that connect two bright
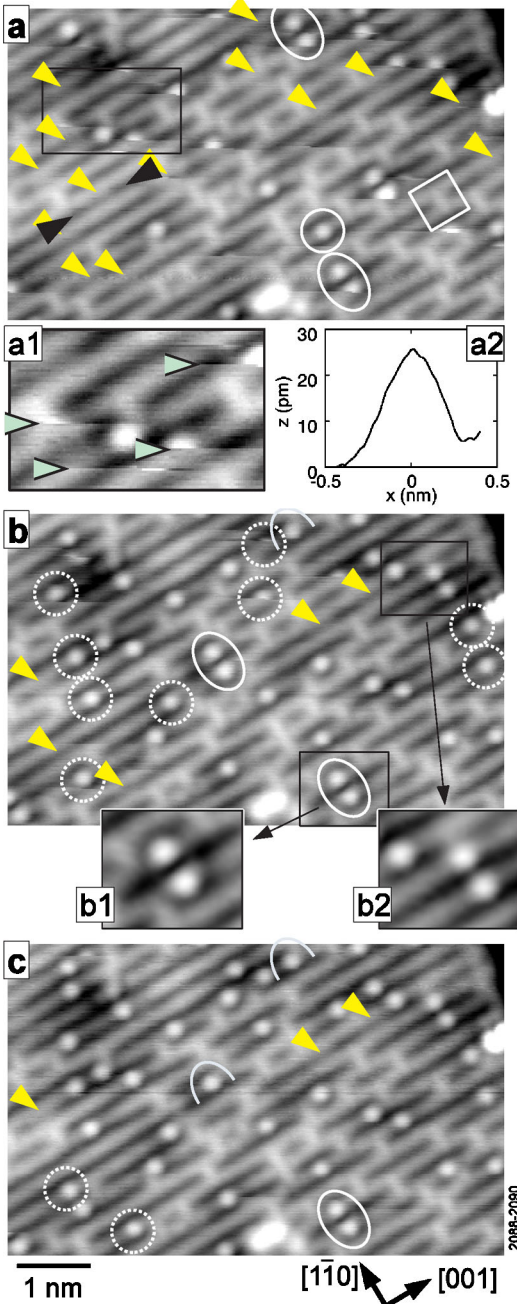
FIG. 1 (color online). Successive STM images ($V_{\text{sample}} = +1.8$ V, $I = 0.05$ nA, $T_{\text{sample}} = 17$ K, 120 seconds per image) of a reduced rutile TiO_2(110) surface after exposure to 0.045 L O_2 at ≈ 100 K. White box: Oxygen vacancy (V_O). Circles: O adatoms (O_{ad}). Dotted circles are O_{ad}'s formed from O_2 in the previous image. Yellow (bright) arrows: Adsorbed O_2. Ovals: Two bean-shaped O_{ad}'s from dissociation of O_2. (a1) Streakiness due to O_{ad} creation (arrows); (a2) averaged line profile across adsorbed O_2 recorded along O_{br} rows (one marked by black arrows). (b1),(b2) Comparison of O_{ad} pairs with and without V_O in between.

Ti_{5c} lines. In Fig. 1(a), 58 V_O's are visible; one is marked with a white box. Reference measurements before O_2 adsorption showed that an image of that size should contain 120 ± 20 V_O's. In addition to V_O's, bright, round spots

are visible on the Ti_{5c} rows that are clearly identifiable as O adatoms; one of these is marked with a circle in Fig. 1(a). Since (almost) each isolated O_{ad} is representative of an O_2 molecule that has dissociated and quenched a V_O [2], the numbers of O_{ad}'s and V_O's should add up to 120, the initial vacancy concentration (0.17 ML). Even when counting the O_{ad}'s partly visible in the image, the actual number, 85, is clearly much less.

The STM image in Fig. 1(a) is streaky in a few places. This is seen more clearly in the zoom-in [Fig. 1(a1)], taken at the position of the black box. The streaks—emphasized by arrows in Fig. 1(a1)—are associated with the creation of additional O_{ad}'s, which appear during scanning. Indeed, the number of O_{ad}'s increases in consecutive STM scans [Figs. 1(b) and 1(c)]. Further inspection of Fig. 1(a) shows an additional feature: At some positions, two neighboring bright Ti_{5c} rows appear smeared out and the O_{br} row between them appears slightly brighter than usual [yellow (bright) arrows]. Figure 2(a) also shows such an area; it seems that an additional, but very faint, species sits on the dark O_{br} rows. The apparent height of these features is about ≈ 25 pm as shown by the line profile [Fig. 1(a2)], averaged over a few such sites such as the one marked by the black arrows in Fig. 1(a). For comparison, the Ti_{5c} rows appear 55 pm higher than the O_{br} rows.

We will now show that these smeared out features are indicative of an O_2 at a V_O. In Fig. 1, they are marked with yellow (bright) arrows. Their number decreases during consecutive scans, while the number of O_{ad}'s increases. There is a clear correlation between the position of the faint O_2 features and the freshly formed O_{ad}'s (dotted circles); each new O_{ad} is located at a Ti_{5c} site next to an O_2 in a previous image.

The STM images in Figs. 1 and 2 show yet another new feature: pairs of bright spots, located at adjacent Ti_{5c} rows. In Fig. 1, these are marked by ovals. Such pairs of bean-shaped adatoms, which form occasionally when we dose O_2 at 100 K, have not been reported before. (Note that the pairs of O_{ad}'s [2] that form when O_2 reacts with a Ti_{int} at
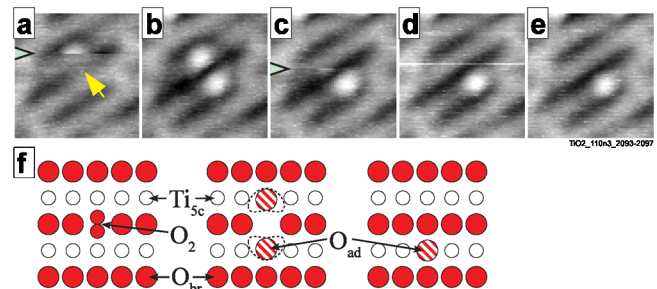

FIG. 2 (color online). Successive STM images ($V_{\text{sample}} = +1.8$ V, $I = 0.03$ nA, $T_{\text{sample}} = 17$ K) of a reduced rutile TiO_2 surface after exposure to 0.045 L O_2 at 100 K. Black arrows point at scan lines where an O_2 molecule is converted into two O_{ad}'s and one of the O_{ad}'s disappears by filling a vacancy. (f) Schematic showing the species involved.

room temperature are located at the same Ti_{5c} row.) Figure 2 shows the creation of such a new adatom pair and its destruction during scanning with the STM. In Fig. 2 (a), the smeared out feature (arrow) corresponding to an O_2 adsorbed at a vacancy site is still present while the tip scans across it. [The slow scan direction is $+y$ (up) in all STM images.] When the tip arrives at the scan line marked at the left edge of Fig. 2(a), the O_{br} row suddenly appears much darker and an adatom materializes on the upper Ti_{5c} row. Figure 2(b) also shows a second, bean-shaped adatom at the opposite side of the original O_2. The upper O adatom disappears in the next frame in Fig. 2(c) (arrow at the edge). Adatom mobility is negligible at 17 K, and inspection of the further surroundings shows that this O_{ad} has not jumped to another location. As soon as the first adatom disappears, the remaining one changes from the original bean shape to the "normal" symmetric and round shape. A few similar cases are marked by ovals and half-ovals in Fig. 1.

Density functional theory-based studies of O_2 adsorbed on $TiO_2(110)$ consistently predict that an O_2^{2-} preferentially sits at an V_O and that the molecule lies flat with its axis perpendicular to the rows. Reference [13] reports Tersoff-Hamann plots of a clean, stoichiometric surface and one with an O_2^{2-} in a V_O. These two plots are remarkably similar to each other, consistent with the claim that the faint, smeared-out features in our STM images are indeed indicative of an O_2 in such a configuration. If this flat-lying O_2 suddenly explodes [25], it is conceivable that the resulting two O's will land on the Ti_{5c} atoms adjacent to the V_O. This is a metastable situation, however; a filled V_O and one O_{ad} will be energetically favored. So one of the O_{ad}'s will migrate back into the now empty V_O and fill it up as shown in the schematics in Fig. 2(f). This process can be induced by the STM tip, as evidenced by the frequent occurrence of partially imaged bean-shaped O_{ad}'s [e.g., Fig. 2(c)].

With the STM we can easily distinguish between an across-the-row, bean-shaped adatom pair that stems from *one* O_2 molecule and a "pair" of two adatoms that have formed independently and sit at adjacent positions on neighboring Ti rows by pure coincidence. For example, the pairs pointed out in Figs. 1(b1) and 1(b2) have a marked difference in shape and brightness. In the first case, the two adatoms are separated by an V_O and in the second case by an O_{br}. This affects the apparent height (brightness) of the adatoms. Interestingly, the image contrast of the V_O between the two O_{ad}'s is also altered. The gap between the two O_{ad}'s in Figs. 2(b) and 1(b1), at the location where we expect the V_O, is quite dark. This is in contrast to the typical appearance of an isolated V_O, which is normally observed as a bright spot on a (dark) O_{br} row. The dark V_O in between the newly formed O_{ad} pair leads to the bean-shaped appearance alluded to above. The STM contrast on TiO_2 is dominated by electronic effects,

and the appearance of this configuration points towards a rearrangement of charge in the vacancy. Based on the extensive theoretical work of the role of excess charge in oxygen adsorption, it seems also conceivable that the adatoms in these two cases—either with or without a V_O between them—do not have the same charge.

The experimental results in Figs. 1 and 2 provide evidence that adsorbed molecular O_2 is indeed observable with STM, but they also point to the facts that the species is very unstable and that the STM measurement itself is the trigger for most of the dissociation that is observed. The results shown here have been taken at 17 K. Additional STM measurements at 78 K show essentially the same features, i.e., O_2 at V_O's, single O_{ad}'s that suddenly appear during scanning, and O_{ad} pairs resulting from the same O_2. STM-induced dissociation at 78 K is even more facile than at 17 K, however, and in many instances most of the dissociation occurs during the first scan of the image. At either temperature, scanning with "harsh" conditions ($V_{sample} \geq +2.4$ V, $I \geq 0.35$ nA) dissociates all O_2's within one single scan, and the density of O_{ad}'s and V_O's approximately equates the number of the original V_O's prior to O_2 adsorption. The effect of the tip is rather localized: When rescanning a slightly shifted area with "milder" conditions, we find that the dissociation occurs within a range of less than ≈ 1 nm from the location of the tip.

What causes the facile dissociation of adsorbed oxygen molecules during the STM scanning? Various mechanisms for tip-induced dynamics are discussed in Ref. [26]. If an antibonding orbital can be accessed by the tunneling electrons, then the rate of dissociation should scale linearly with the tunneling current I. If local heating is responsible, the rate should scale as I^n with a higher value of n. We ran extensive tests, where we varied the tunneling current over more than an order of magnitude (0.004–0.05 nA) but kept all other experimental parameters constant. We chose a tunneling voltage of 1.3 V, the lowest value where reproducible images could be obtained. While we found a large scatter of the adatom creation range (0.0077 ML/scan, standard deviation 0.0035 ML/scan), the adatom creation rate shows no correlation with the tunneling current. This clearly rules out an electron-induced process for the oxygen dissociation. As we observe at most a weak dependence on the tunneling current, by ignoring van der Waals interactions, the interaction between tip and adsorbed O_2 must be due to the electric field, which varies with the distance and, hence, the logarithm of the current. As the change of the shape and composition of the STM tip is not under our control, the local field under the STM tip also changes, even when we use the same tunneling voltage, explaining the scatter of adatom creation rate observed. Hence we propose that the field is the decisive factor in how readily an adsorbed O_2 dissociates. Possibly, the STM tip pushes the O_2 molecule into a configuration that allows

an easy dissociation. Exactly what this configuration might be is unclear at this point, but we consider it likely that a position closer to a Ti atom in the substrate will facilitate dissociation. It should be emphasized, however, that the product of any tip-induced process can be observed only when it is (meta)stable on the surface. In other words, the tip helps overcome a barrier. We consider it likely that this process also happens spontaneously at higher temperatures, and, thus, the observed O_{ad} pairs should be considered the reaction intermediate of O_2 dissociation at $TiO_2(110)$.

Desorption measurements have shown that the dissociation probability of O_2^{ad}'s is coverage-dependent and that small amounts of O_2 (the coverage regime of the STM measurements shown here) dissociate more easily than larger coverages [5]. We have varied the O_2 exposure in our measurements as well, but we did not observe any new features or any significant differences in adatom creation. Very recent stimulated desorption by photons and thermal desorption work [4] has shown that irradiation with above-band-gap photons not only desorbs O_2 (through hole capture) but also dissociates O_2 through an electron-mediated process. In addition, photon exposure was also reported to create a "photoblind," thermally stable molecular O_2 species [4], which was again attributed to tetraoxygen. We have searched for such species by dosing higher amounts of O_2 and irradiating the sample with a UV-light-emitting diode (365 nm, $\approx 10^{15}$ photons cm^{-2} s^{-1}), but, again, no evidence could be found for such a species.

In summary, we have unequivocally observed molecular O_2 adsorbed at oxygen vacancies on TiO_2 with low-temperature scanning tunneling microscopy. Our measurements also show the difficulty of using STM as an analytical tool for learning more about this species: The STM measurement invariably dissociates the molecule even at the smallest tunneling currents, albeit with a probability that is highly tip-dependent. While it is fascinating to directly observe this dissociation, it is a nuisance when one wants to learn more about the adsorbed O_2 molecule itself. The STM contrast of an O_2 in a V_O is so faint that it is easily overlooked in a somewhat noisier instrument. On the other hand, the creation probability of the O adatoms is tip-dependent; thus, a mere counting of the adatoms needs to be conducted carefully to avoid erroneous conclusions.

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*Present address: Department of Physics, University of California, Berkeley, CA, USA.
†diebold@iap.tuwien.ac.at

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