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DISSERTATION

DEFECTS AND ADSORPTION AT TITANIUM DIOXIDE SURFACES

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"The quality of STM images is directly proportional to your ability to shift your frustration tolerance level" - Dr. Evil

Abstract

Defects and Adsorption at Titanium Dioxide Surfaces

 TiO_2 is one of the most investigated metal oxide in surface science. Three stable polymorphs are known: rutile, anatase and brookite. From an applied, and from the catalysis point of view, rutile and anatase are the more interesting systems. TiO_2 is used in a wide range of applications; in heterogeneous catalysis, in solar cells, as gas sensors, as a white pigment in paints and cosmetic products, as optical coating or in biocompatible implants. A basic, but important process for catalysis is the adsorption of gases on surfaces. Some important examples are investigated in this thesis using low-temperature Scanning Tunneling Microscopy (LT-STM). A freshly prepared TiO_2 rutile (110) surface always contains - depending on the degree of reduction - a certain amount of bridging oxygen vacancies, which facilitate the adsorption at these surface defects. When the clean surface is exposed to molecular oxygen at ambient temperature, the adsorption path is the following: molecular oxygen is adsorbed, dissociates and one oxygen atom of the molecule fills a bridging oxygen vacancy, while the second one forms an adatom on the neighboring five-fold titanium row. This adatom is strongly bound, and can be desorbed either thermally or by using pulsed laser light with a wavelength of 355 nm. However, when the oxygen adsorption is done at 100 K, the molecules are adsorbed in bridging oxygen vacancies as molecules. These are identified in STM images as very faint changes of contrast along the bridging oxygen rows, if the tunneling parameters are very gentle (+1.3 V sample bias and tunneling)currents lower than 0.1 nA) and the temperature of the crystal is at 17K during scanning. Using these conditions an intermediate, metastable configuration of the adsorbed oxygen molecule can be imaged. Scanning the surface at higher voltage and/or current results in dissociation of the adsorbed molecules within one single scan. Also scanning the adsorbed molecules at higher temperatures (e.g., 77 K) results in immediate dissociation.

Another – from the catalysis point of view – important gas is carbon monoxide. Adsorption studies show that this molecule sticks to the bridging oxygen vacancies and also to the five-fold coordinated titanium surface atoms. CO has a high sticking probability on the TiO_2 rutile (110) surface and a dose of 15 Langmuir (L) of CO forms a full monolayer on the surface.

For the technologically most interesting anatase polymorph, single crystals are hard to obtain. Most studies have been performed using powder materials. Now, larger single crystals are available. The second part of this thesis investigates an anatase mineral sample. As long as the crystal is not reduced too much, the preparation of a clean, flat TiO₂ anatase (101) surface with large terraces is possible by performing sputtering and annealing cycles. With increasing number of preparation cycles and therefore increasing degree of reduction, the size of the terraces drops. This makes it necessary to periodically reoxidize the crystal at high temperature. After reoxidation, a rough structure on the TiO₂ anatase (101) surface could be imaged with STM. Subsequent annealing in UHV is a good way to remove the latter and obtain the clean TiO₂ anatase (101) surface with large terraces. In contrast to the rutile surface, DFT calculations predicted for the anatase surface that oxygen vacancies

are less stable on the surface than in the bulk. However, at low temperature (105 K) they can be created by electron bombardment. At this temperature, they are stabilized on the surface, and can be imaged with STM. When the crystal is then heated to temperatures higher than 200 K, the number of surface oxygen defects decreases due to migration into the bulk. For each temperature, there exists a dynamic equilibrium of defects migrating from the surface to the subsurface region and also in the inverse direction. The hopping rate of the defects to and from the surface depends on the temperature and is higher for higher temperatures.

Adsorption of the same two gases, namely oxygen and carbon monoxide, was tested on TiO_2 anatase (101) as well. Oxygen adsorbs at two different positions on the TiO_2 anatase (101) surface. If adsorbed on two-fold coordinated oxygen atom positions, it is observed as a dimer-like feature in STM images, while if adsorbed on the five-fold coordinates titanium atoms, its appearance in STM images is star-like. By dosing large amounts of oxygen, a coverage of 2.5% of a monolayer can be achieved. When the oxygen-dosed surface is heated to ambient temperature and higher, first the star-like features change their shape and at temperatures higher than 450 K new extra bright features appear in STM images, which are interpreted as precursors of an annealing process.

Another interesting experiment is the adsorption of carbon monoxide. In STM images recorded using very gentle tunneling conditions (1.3 V and currents lower than 0.06 nA), the preferred adsorption position of the CO molecule on the surface could be identified as the five-fold coordinated surface titanium atoms. It is only weakly bound and the STM tip can easily induce surface diffusion of the CO molecules. CO can also be thermally desorbed by heating the crystal to temperatures higher than 150 K. Again the sticking coefficient of CO is very high. In comparison to oxygen it is larger by a factor of 5000, which poses a problem in oxygen adsorption measurements, because CO is easily desorbed from the inner walls of the UHV chamber and adsorbs on the sample.

Kurzfassung

Defekte und Adsorption auf Titandioxidoberflächen

TiO₂ ist ein sehr intensiv untersuchter Vertreter der Metalloxide. Von TiO₂ sind drei stabile Kristallmodifikationen bekannt, nämlich Rutil, Anatas und Brookit. Während Rutil und Anatas sowohl vom Standpunkt der technischen Anwendungen, als auch vom wissenschaftlichen Standpunkt betrachtet, äußerst interessant sind, spielt Brookit eine untergeordnete Rolle. Nicht nur Kristalle, sondern hauptsächlich TiO_2 Pulver finden in vielfältiger Weise Anwendung, zum Beispiel in der heterogenen Katalyse, in Solarzellen, als Gassensoren, als weiße Pigmente in Farben und vielen kosmetischen Produkten, als optische Beschichtung zur Vergütung von Linsen oder auch in der Medizin für biokompatible Implantate. Ein elementarer, aber vor allem für die Katalyse sehr wichtiger Prozess ist die Adsorption von Gasen auf einer Oberfläche. Eine frisch präparierte Rutil (110) Oberfläche enthält immer eine bestimmte Anzahl von Brückensauerstofffehlstellen, die vom Reduktionsgrad des Kristalls abhängt. Diese Fehlstellen ermöglichen die Adsorption auf der Oberfläche. Diese Fehlstellen und die Adsorption von Gasatomen werden wurden mit dem Rastertunnelmikroskop (STM) untersucht. Wenn eine reine TiO₂ Rutil (110) Oberfläche bei Raumtemperatur molekularem Sauerstoff ausgesetzt wird, können Sauerstoffmoleküle adsorbiert, und auch dissoziiert werden. Ein Sauerstoffatom des Moleküls füllt dann die Fehlstelle auf, während das andere Sauerstoffatom als Adatom auf der benachbarten Titanreihe gebunden wird. Das so entstandene Adatom ist stark gebunden und kann entweder thermisch oder zum Beispiel mittels eines Laserpulses mit geeigneter Wellenlänge (355 nm) von der Oberfläche desorbiert werden. Erfolgt die Sauerstoffadsorption allerdings bei 105 K, können intakte Moleküle in den Brückensauerstofffehlstellen gebunden werden. Diese Moleküle sind auch in STM Bildern als sehr schwache Kontraständerung entlang der Brückensauerstoffreihen identifizierbar. Allerdings ist es dazu zwingend notwendig, äußerst sanfte Tunnelbedingungen zu wählen (Probenspannung +1.3 V und Tunnelströme geringer als 0.1 nA). Außerdem ist es zusätzlich erforderlich, die Probe auf eine Temperatur von nur 17 K abzukühlen. Unter diesen Bedingungen ist nicht nur die Abbildung der adsorbierten Sauerstoffmoleküle in den Brückensauerstofffehlstellen möglich, sondern auch ein metastabiler Zwischenzustand, der sich bei der Dissoziation einstellt, kann beobachtet werden. Wenn die Oberfläche mit höheren Spannungen oder Strömen abgetastet wird, dissoziieren fast alle adsorbierten Moleküle bereits beim ersten Abtasten der Oberfläche. Derselbe Effekt tritt auch auf, wenn man versucht das Experiment bei höheren Temperaturen (z.B.: 77 K) durchzuführen. Ein weiteres technisch wichtiges Gas, dessen Adsorptionsverhalten interessant ist, ist Kohlenmonoxid. In Adsorptionsstudien auf einer reinen Rutil (110) Oberfläche konnte nachgewiesen werden, dass das CO Molekül auf den Brückensauerstofffehlstellen und den Oberflächentitanatomen adsorbiert. Außerdem ist schon niedrige Dose von CO (15 Langmuir (L)) ausreichend, um praktisch eine vollständige Monolage auf der Oberfläche zu bilden.

Vom Standpunkt der Katalyse aus gesehen ist die Anatas Kristallmodifikation die effektivere. Leider waren lange Zeit keine Anatase-Einkristalle von ausreichender Größe für STM Untersuchungen verfügbar, sodass die bereits bekannten Daten von indirekten Untersuchungsmethoden stammen. Kristalle in ausreichender Größe sind nun verfügbar und solange sie nicht allzu stark reduziert sind, auch leicht zu präparieren. Normalerweise reicht ein Zyklus bestehend aus einmaligem Ionenbeschuss und anschließendem Heizen im Ultrahochvakuum aus, um eine flache Anatase (101) Oberfläche mit großen Terrassen zu erhalten. Mit steigendem Reduktionsgrad allerdings sinkt die Terrassengröße und eine Reoxidation des Kristalls bei hoher Temperatur wird notwendig. Nach der Reoxidation ist auf STM Bildern oft eine Überstruktur erkennbar, die aber durch Heizen im UHV wieder verschwindet. DFT Simulationen haben gezeigt, dass im Gegensatz zur Rutil (110) Oberfläche Sauerstofffehlstellen auf der Anatase (101) Oberfläche nicht so stabil sind wie in der Lage darunter. Fehlstellen in der Oberfläche können trotzdem durch Beschuss mit niederenergetischen Elektronen erzeugt werden und werden, wenn der Beschuss bei tiefen Temperaturen (105 K) erfolgt, und bleiben an der Oberfläche stabil. Wird der Kristall anschließend auf unterschiedliche Temperaturen geheizt, sinkt die Dichte der Sauerstofffehlstellen auf der Oberfläche ab einer Temperatur von 200 K merklich. Es stellt sich jeweils ein dynamisches, und von der jeweiligen Temperatur abhängiges, Gleichgewicht zwischen auf die Oberfläche wandernden, und den diese in Richtung Kristallvolumen verlassenden Fehlstellen ein. Allgemein ist die Sprungrate von Defekten auf die Oberfläche und in das Volumen bei höherer Temperatur größer. Um das Verhalten der Anatase (101) Oberfläche in Bezug auf die Adsorption von Gasen zu testen, wurde zuerst eine reine Kristalloberfläche präpariert, auf die dann verschiedene Gase dosiert wurden. Sauerstoff adsorbiert an zwei verschiedenen Stellen auf der Anatase (101) Oberfläche: Eine Adsorptionsposition ist an Stelle der zweifach-koordinierten Oberflächensauerstoffatome, die zweite ist auf den fünffach-koordinierten Oberflächentitanatomen. An der ersten Position adsorbierte Sauerstoffmoleküle erscheinen auf STM Bildern als helle Dimerstruktur, während auf Titanatomen adsorbierter Sauerstoff im STM sternförmig erscheint. Die Exposition der reinen Anatase (101) Oberfläche mit hohen Dosen von Sauerstoff führt zu einer Bedeckung von circa 2,5% einer Monolage. Bei der Erwärmung einer zuvor mit Sauerstoff behandelten Anatase (101) Oberfläche auf Raumtemperatur ändern zuerst die in STM Bildern sternförmig erscheinenden Sauerstoffmolekule ihre Form, und bei weiterer Erwärmung auf Temperaturen höher als 450 K treten neue sehr helle Objekte auf. Diese können als Vorläufer des Ausheilprozesses der Oberfläche interpretiert werden.

Ein weiters interessantes Experiment ist die Adsorption von Kohlenmonoxid. Wird CO auf der Anatase (101) Oberfläche adsobiert, kann aus STM Bildern, die mit sehr sanften Tunnelbedingungen (Probenspannung +1,3 V und Tunnelströme geringer als 0,06 nA) aufgezeichnet werden, geschlossen werden, dass der bevorzugte Adsorptionsplatz des CO Moleküls am fünffach-koordinierten Oberflächentitanatom ist. Da es dort nur sehr schwach gebunden ist, kann es leicht mit der STM Spitze zur Diffusion über die Kristalloberfläche angeregt werden. Eine Temperatur von 150 K reicht schon aus, um CO wieder von der Oberfläche zu entfernen. Allerdings ist der Haftkoeffizient von CO sehr hoch. Im Vergleich zu Sauerstoff ist er um einen Faktor 5000 höher, was bei der Adsorption von Sauerstoff ein Problem darstellt. CO kann leicht von den Innenwänden der UHV Anlage desorbiert werden und gelangt so auf die Kristalloberfläche.

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Chapter 1 Introduction

1.1 Preamble

Concerning the possibility of watching any reactions or processes, the human eye is limited in its abilities. When reactants are too small to be seen with bare eyes – like atoms – a magnifying glass or better a microscope is used for "amplification" of its natural properties. Other limitations are the speed and visibility of a chemical or physical reaction. Some reactions are taking place in an environment, which is not accessible for humans, or are simply too fast. In this case the use of a camera can provide a solution, and by increasing the number of images recorded by the camera per second, one gets what is usually understood as "slow motion" recording.

In order to carry out the experiments described in this work it was necessary to combine all of the above mentioned methods to study what is happening on the surface of a single crystal at atomic scale. For direct observation of the atoms one needs a scanning tunneling microscope (STM), which is used in an ultra high vacuum environment in order to keep the surface – at least for the time of the experiment – clean. But this tool is unfortunately limited in its recording speed. So the trick was to find another parameter, which could be tuned, to get access to the timescale, at which the reactions take place. In this case "slow motion" was not realized by increasing the frame rate of the recording device – which is the general understanding of "slow motion" – but decreasing the speed of reactions by cooling the whole system, where the reaction takes place and recording time-lapse images, which could then be put together to form a "movie".

This thesis presents STM studies of different modifications of TiO_2 single crystals. Chapter 2 gives an introduction to the properties of the TiO_2 rutile (110) and TiO_2 anatase (101) crystals and also includes a short overview of the experiments done earlier. In addition to this still open questions are mentioned.

In the following chapter 3, surface analytical techniques used in this work will be presented. A basic introduction to these methods is given there, to provide the possibility to the reader to follow the results and conclusions presented later. Chapter 3 also contains short descriptions of the setups at the TU Wien, where the experiments have been performed.

Chapter 4 gives a detailed report of the experiments done on the TiO_2 rutile (110) surface. It starts with the characterization of the sample, and then continues with the investigation of the oxygen adsorption process on this surface. These experiments were carried out at two different temperatures (17 and 78 K, respectively) and the surface chemical reactions are analyzed in time-lapse STM images. This also allowed us to obtain mechanistic models for the single reaction steps; some of the results were published in reference [1].

In the following chapter 5 the anatase polymorph of TiO_2 is investigated. Again the sample is characterized, and we describe how we provide a clean surface with large terraces as a reproducible starting point for the following experiments. This part also includes a short study about CO adsorption on the TiO_2 anatase (101) surface, where the preferred adsorption position on the TiO_2 anatase (101) surface and the desorption properties are determined. In another series of experiments the surface is irradiated with low energy electrons to create surface oxygen vacancies. These are then analyzed with respect to their thermal stability and their diffusion behavior. An article based on these results was published in reference [2]. The next part of chapter 5 presents studies on oxygen adsorption on the pristine TiO_2 anatase (101) surface. The different features visible in STM images and their thermal stability are presented. The last part in this chapter combines there two experiments. In a first step, surface defects are created at the clean TiO_2 anatase (101) surface and then oxygen is adsorbed on this defective surface.

In the conclusions (chapter 6) all results, which are presented in the previous chapters are summarized.

Chapter 2 Fundamentals

Titanium dioxide was first discovered by William Gregor, an amateur chemist. He performed experiments with sands from a local river in Cornwall and found a black substance similar to gunpowder. After several experiments he concluded that he found the oxide of a new element: Menachanite. This finding did not receive much attention, but in 1795 Martin Heinrich Klaproth could isolate rutile from Hungarian red schorl and found a similarity with the material discovered by Gregor. He removed iron and another major component and named it "Titanium", after the mythological titans [3].

In 1972 a seminal article [4] was published by Fujishima and Honda, which reported the photolysis of water on TiO_2 electrodes without applying an external bias. This started an avalanche of research, because TiO_2 is inexpensive and also single crystals for scientific research were readily available. In addition to this, TiO_2 shows – in contrast to *i.e.*, ZnO - no photocorrasion. These authors already claimed that surface states play an important role in this process. Today, TiO_2 is heavily used in many different applications. Although the quantum yield for the chemical conversion of sunlight into electrical energy is rather low, TiO_2 is used in this field. The perhaps most interesting application of TiO_2 is the decomposition of organic molecules using photocatalysis. Upon irradiation of TiO_2 with sunlight, an electron-hole pair is formed, which can thereafter separate and the electron and the hole can migrate to the surface and react with adsorbed water and oxygen. The latter become highly reactive radicals species and can – sometimes in several reaction steps – decompose organic molecules into carbon dioxide and water [5, 6, 7]. This process has a wide range of applications, from self cleaning coatings on walls or cars to medical instruments, which can be sterilized by shining UV light on them. Other applications include gas sensors, where the change in the electric signal of TiO_2 is used to detect adsorbed oxidizing or reducing gases, or simply as a white pigment in the paint industry. For improving the performance of TiO_2 in these applications and applying this material to a new field, it is absolutely necessary to have a profound knowledge of the relationship between its surfaces and its chemical and physical properties. These properties include the geometric and electronic structure and the very important properties related to defects. In addition it is important to understand how elementary adsorption and desorption processes work on the TiO₂ surface. Due to its ready availability in sufficiently pure form, and wellestablished preparation recipes, TiO_2 is one of the most investigated metal oxide systems in surface science (see reference [8]). A short review of into the properties and the already known physics taking place on TiO_2 surfaces is given in the following paragraphs.

At ambient conditions, TiO_2 can be found in three (at least meta-)stable polymorphs: rutile, anatase and brookite. Rutile and anatase play a major role in both science and technical applications [8, 9], therefore only these are described in more detail here. Rutile and anatase are constructed of nearly octahedral units. These octahedra consist of a titanium atom in the center surrounded by six oxygen atoms. Both polymorphs have in common that the octahedra are elongated in both directions of the polar axis (see reference [10]), in order to reduce the total energy of the complex. This Jahn-Teller distortion also splits the molecular orbitals and the orbital degeneration vanishes [11].

In rutile crystals, the long axis of neighboring octahedra are tilted by 90 degrees with respect to each other, and they share a corner along the <110> directions. The oxygen atoms are coordinated by three titanium atoms in a distorted trigonal-pyramidal geometry. In anatase crystals the corner-sharing octahedra form (001) planes, which are connected with their edges with the plane of octahedra below. In contrast to rutile, each octahedron shares four edges with neighboring octahedra instead of two in rutile crystals. [10].

Both polymorphs have in common that the oxygen atoms in the bulk are three-fold coordinated [8]. Perfectly stoichiometric oxide surfaces are chemically rather inert, but if surface defects are present, the reactivity significantly rises. At this point another difference between the two polymorphs is noteworthy: When treated in a similar way, the density of surface oxygen defects on rutile surfaces is significantly higher than on anatase surfaces [8], as has recently been found by our group. In scientific research the rutile polymorph of TiO_2 is mainly used, because of its easy availability and the fact that a clean surface is easy to prepare. However, anatase is used in most applications of TiO_2 , because in powders a larger fraction of anatase compared to rutile can be achieved [12]. Until now, STM studies of the anatase surfaces are rather rare.

Despite the extremely low pressure in UHV systems, there are enough gas molecules in the residual gas to adsorb on previously cleaned crystal surfaces. These have to be removed regularly. TiO₂ crystals were cleaned before each experiment by sputtering and subsequent annealing to let the surface relax and form large terraces suitable for STM analysis. By sputtering, oxygen atoms are preferentially removed from the surface, *i.e.*, the crystal is reduced. This process induces color centers and the crystal's color changes from transparent into different shades of blue, depending on how strongly the crystal is reduced [13]. The higher the grade of reduction, the higher becomes the conductivity, which is governed by n-type doping via intrinsic defects.

These defects are very important for the crystal's properties. As mentioned above, photocatalysis on the surface of a semiconductor depends on the creation of electron-hole pairs within the crystal. After creation of these pairs, the excited charge carriers diffuse to the surface and can there initiate different chemical reactions. However, electron-hole recombination reduces the efficiency of the pair creation process. At this point the defect states within the crystal play an important role, because they influence the parameters of the electron-hole creation and diffusion [14, 15]. In reference [14] it is concluded that an oxygen vacancy in anatase induces a shallow, highly energetic and strongly delocalized energy level together with a strongly localized deep one. In contrast, in rutile, an oxygen vacancy induces only a strongly localized deep level, which contributes to explain the observed differences between the two polymorphs.

Via annealing, the sputtered TiO_2 surface is restored by migration of the excess titanium atoms into the bulk [16]. However, even after annealing there are defects present in TiO_2 crystals. In rutile crystals, oxygen vacancies remain on the surface. In the bulk, titanium interstitial atoms are the dominant defect type. These interstitials introduce donor states close to the conduction band and therefore shift the electrochemical potential (*i.e.*, Fermi level), which results in a higher conductivity. Within the bulk of the rutile crystal interstitials can diffuse relatively easy. In rutile crystals titanium interstitial atoms use the free space along the [001] direction, while oxygen atoms in the bulk migrate via a site exchange processes with other atoms [8].

In general, surface defects are the active centers for *e.g.*, adsorption reactions [17, 18]. Therefore it is necessary to know how these reactions exactly take place on the defective surfaces and how to create surface defects.

These issues are addressed for TiO_2 rutile (110), where surface defects – bridging oxygen vacancies – are well-understood. Here the dissociation of an oxygen molecule on a vacancy is investigated.

For anatase, the situation is different. While oxygen vacancies are energetically stable on the surface of rutile crystals, DFT-studies have proposed that they are energetically more stable in the subsurface region of anatase crystals (see reference [19]). In this reference also the diffusion energies for titanium interstitial atoms and oxygen vacancies are calculated. The potential energy barriers for titanium interstitial atoms are between 0.45 and 0.75 eV for the [301] and [001] direction, respectively. For oxygen vacancies, the diffusion barriers inside the bulk are in the same range as the ones for titanium interstitial atoms. In this work the activation energies for subsurface migration of surface oxygen vacancies are studied. For this purpose Electron Stimulated Desorption (ESD) turned out to be the ideal technique to create surface oxygen vacancies on the TiO₂ anatase (101) surface, as surface oxygen vacancies can be produced non-thermally at low temperatures. In follow-up experiments also the adsorption of oxygen on surface and subsurface vacancies on the TiO₂ anatase (101) surface is investigated.

2.1 Rutile

Due to the availability of well polished, large, and inexpensive single crystals, rutile is the (experimentally) most investigated and characterized form of TiO₂ in surface science. Rutile crystallizes in the tetragonal D_{4h}^{14} -P4₂ nm space group [8] and its crystallographic parameters have been determined in reference [20] as a = b = 0.4594 nm, c = 0.2959 nm. Electronically, rutile is a wide bandgap semiconductor with a gap of 3 eV. The bands of the crystal are dominated by Ti3d (conduction band) and O2p (valence band) states. In general, TiO₂ rutile is an ionic semiconductor with a rather strong covalent character [21].

2.1.1 The Rutile (110) Surface

Rutile exposes several stable surfaces, and surface energy calculations showed that the (110) facet has the lowest energy, the (001) the highest [22].



Figure 2.1: Ball and stick model of the TiO_2 rutile (110) surface. Titanium (blue), oxygen (red) and bridging oxygen (O_{br} ; dark red) atoms. In addition the most common defects (O_{vac} 's) are visible. An oxygen adatom (purple) and hydrogen atom (green) forming an OH group on the surface are shown as well.

The (110) surface is bulk terminated and non polar (Tasker type II) [23]. Due to the partially covalent character of the bonding, the stability of the surface is also governed by breaking the least number of bonds and the longest ones in the structure [24]. On the surface, rows of five-fold coordinated titanium atoms are separated from rows of sixfold coordinated titanium atoms by rows of three-fold coordinated oxygen atoms in [001] direction forming a Tasker Type II non-polar surface [23]. While the five-fold coordinated titanium atoms are exposed to the vacuum, the six-fold coordinated ones are covered by rows of "bridging" oxygen atoms, which atoms are two-fold coordinated. The dimensions of the surface unit cell are the following: 2.96 Å in [001] direction and 6.5 Å in $[1\overline{1}0]$ [24]. Common defects on the clean TiO_2 rutile (110) surface, which can be easily identified in STM images, are step edges, line defects, such as " 1×2 rows", and (on very reduced samples) crystallographic shear planes (see also [8]). For this work the most interesting defects are bridging oxygen vacancies (O_{vac}) . These are always present on freshly prepared surfaces for the following reasons. They are formed when the crystal is heated to high temperatures (e.g., 1100 K like in reference [25]), when top layer titanium atoms and bulk oxygen vacancies diffuse to equilibrate with the whole bulk-recuced crystal [16, 25]. Every sputtering / UHV annealing cycle increases the degree of reduction and therefore the number of bridging oxygen vacancies increases. In reference [26] a method was suggested to "reoxidize" the crystal. Instead of normal UHV annealing, the crystal is heated and exposed to an oxygen atmosphere for a long time, which decreases the degree of reduction and the number of bridging oxygen vacancies. If this is done extensively, the color of the crystal can also be changed back from dark blue to transparent [8].

The TiO₂ rutile (110) surface was studied with STM already in the 1990's. Atomic resolution was available, but it took several years to develop the correct interpretation of the data [27]. In most cases STM images are recorded at positive sample bias (empty states tunneling). On the images of the TiO₂ rutile (110) surface, bright and dark rows alternate. Although the oxygen atoms are geometrically closer to the STM tip, they appear dark, while the titanium atoms, though located further away, form the bright rows. This inverse contrast is explained by the electronic structure of the surface, where the tip follows lines of constant local density of electronic states (LDOS; see section 3.1.1, below). Above the titanium atoms the LDOS is greater than above the oxygen atoms [27]. Figure 2.2 shows two STM images of the clean TiO₂ rutile (110) surface. Figure 2.2(a) shows the surface with small terraces, and only very few defects.



(a) Imaging parameters: $40 \times 40 \text{ nm}^2$; 1.22 V, 0.27 nA, 79.1 K

(b) Atomically resolved STM image of the TiO_2 rutile (110) surface. Red box: $O_{\rm vac}$, blue box: hydroxyl adsorbed in a $O_{\rm vac}$, orange box: oxygen adatom. Imaging parameters: $6 \times 6 nm^2$; 1.61 V, 0.79 nA, 78.5 K

Figure 2.2: STM images of the TiO_2 rutile (110) surface. All STM images presented in this work are listed in the Appendix section 7.1 together with the image location on the LT-STM lab Sun STM computer.

The above mentioned bridging oxygen vacancies are visible in STM images as bright features, located on the dark rows and connecting two adjacent bright titanium rows (see Figures 2.2 and 2.3).

If there is any water in the chamber, which can reach the sample, the water molecules dissociate at an oxygen vacancy [28, 29]. The result is two adjacent hydroxyl groups on the surface, which are believed to have different activation energy barriers for surface diffusion [30]. Hydroxyl groups on the surface are easily identified in STM images as bright spots

on the bridging oxygen rows. In comparison to bridging oxygen vacancies the difference in contrast is clear, as shown in the STM image in Figures 2.2(b) 2.3.



Figure 2.3: Common defects due to water dissociation at O_{vac} 's on a sputtered and annealed TiO_2 rutile (110) surface. red box: O_{vac} , blue box: hydroxyl adsorbed in a O_{vac} , black box: oxygen adatom on a Ti_{5c} atom, green box: terminal OH on a Ti_{5c} atom. Imaging parameters: $40 \times 40 \text{ nm}^2$, 1.5 V, 0.29 nA, 78 K

In reference [31] the existence of a terminal OH group was reported, which means that an OH molecule is bound to a five-fold coordinated surface titanium atom. Another remarkable and important feature on the TiO_2 rutile (110) surface is adsorbed atomic oxygen. Adsorbed oxygen on TiO_2 can play two different key roles in photocatalysis: On the one hand as oxidative species, and on the other as an electron scavenger. In heterogeneous catalysis it is important for low temperature oxidation processes, while in semiconductor-based gas sensors its strong influence on the conductivity is a major aspect for the sensitivity of the sensors. These – among others – are good reasons to study the interaction of the TiO_2 surface with oxygen from a fundamental point of view. Much fundamental research of the interaction of oxygen with the TiO_2 surface has already been done in the past (see references [8, 32, 17, 26, 33, 34, 35, 36, 37, 38, 39, 40, 41, 42, 43, 44, 45, 46, 47, 48, 49, 50]). From the large number of articles, which were published on this model system, one would think that this system is already well known, and the processes taking place on the TiO_2 rutile (110) surface are well understood. Nevertheless, there are still some gaps to fill in the understanding of fundamental processes.

If a stoichiometric TiO_2 rutile (110) surface is exposed to oxygen, the latter can only be weakly physisorbed, and no chemical bond is formed. It was shown in reference [46] that physisorbed O₂ desorbs below approximately 75 K. This experimental study is in good agreement with predictions from density functional theory (DFT)-based calculations. Theorists report that excess charge, *i.e.*, a surface with at least some bridging oxygen vacancies or titanium interstitial atoms is inherently needed for the chemisorption of O_2 (see references [43, 47, 51]). The chemisorption of oxygen on a defective TiO_2 rutile (110) surface has already been studied using desorption techniques. However, the adsorption process itself cannot be studied in TPD (Temperature Programmed Desorption) experiments, because the mass spectrometer only sees what is desorbed, and no direct image of the surface and the process itself can be gained. To gain information about this process, STM studies are a powerful tool. A study reported in reference [47] describes the dissociation of oxygen molecules adsorbed on five-fold coordinated titanium atoms. Other references report the formation of a new species composed of four oxygen atoms [35]. But the mechanism of the oxygen adsorption of an oxygen molecule in a surface oxygen vacancy and its dissociation is still an open question, which will be discussed in this work (see sections 4.3.1 and 4.3.2). Another interesting fact was described in [26, 49, 50]: it was found that at elevated temperatures interstitial titanium atoms become mobile, and migrate to the surface. If oxygen is present, both species can react to form excess TiO_x . It is a regrowth process, but in many cases there is no stoichiometric TiO_2 formed until the crystal is annealed in UHV at temperatures above 900 K. What happens at low temperature is less clear, however. When molecular oxygen is dosed on a cold sample, typically at a temperature around 100 K, various desorption techniques – thermal desorption (TPD) as well as stimulated desorption by electrons (ESD) or photons (PSD) – consistently show the formation of a chemisorbed, molecular precursor [17, 35, 36, 37, 38]. It was reported in references [17, 38] that there are two different adsorption states for molecular oxygen on bridging oxygen vacancy sites. One is formed, when the adsorption takes place at 105 K. These authors report that molecules adsorbed in this way can be photo-activated for the oxidation of CO to CO_2 . The other form is inactive for photo-oxidation of CO and undergoes faster desorption. Further it was claimed that the first, photo-active state can irreversibly be transformed into the second by heating up to 250 K.

This thesis presents results of oxygen adsorption at 105 K on a clean TiO_2 rutile (110) surface. According to reference [52] oxygen chemisorbs at this temperature as a molecule on the TiO_2 rutile (110) surface.

References [17, 38, 40, 41] report that the oxygen molecule is negatively charged, likely resembling a peroxide $O_2^{2^-}$ ion, and that the process of stimulated desorption is holemediated. One interesting, and somehow mysterious aspect of these experiments, however, is the fact that some of this molecular oxygen desorbs at temperatures well above room temperature ≈ 400 K [35, 36, 53]. Based on TPD and ESD measurements, Kimmel and Petrik [35] postulated the formation of a stable $O_2^{2^-}$ species ("tetraoxygen") that survives up to these high temperatures without dissociating.

Reference [45] reports DFT-based calculations of different amounts of molecular oxygen adsorbed on a TiO₂ rutile (110) surface. According to these calculations, up to three oxygen molecules can be adsorbed per bridging oxygen vacancy. Two of the adsorbed molecules are predicted to form a stable complex ("tetraoxygen", O_4^{2-}), which allows the adsorption of the third molecule. In addition to this the authors report the existence of different charge states of the adsorbed O₂ and (O₂)₂ (tetraoxygen) species, which may influence the



Figure 2.4: Side- and top view of the TiO_2 rutile (110) surface with different amounts of adsorbed oxygen molecules in the lowest energy configurations. The sketches show (a) one, (b) two and (c) three adsorbed oxygen molecules per O_{vac} . The numbers show the calculated bond lengths, which are given in Å; Yellow, red and gray balls represent adsorbed oxygen, surface oxygen, and titanium atoms, respectively. Image taken from [45].

reactivity of O_2 to photo-induced CO oxidation.

Nevertheless, the mechanism of oxygen dissociation at lower temperatures has not yet been observed with STM. However, there also does not exist any STM study to prove the existence of the proposed "tetraoxygen" postulated in reference [35], which was postulated due to desorption studies. These topics are studied with STM in this thesis, which gives a direct real space image of the surface. Another advantage of an STM analysis of this topic is the possibility to record series of time-lapse STM images, which can provide information about the dynamics of the adsorption and dissociation process. Thus, one should also emphasize that molecular oxygen on TiO₂ was never directly observed with STM previously. In reference [54] calculated configurations of molecular and dissociated oxygen on the TiO₂ rutile (110) surface are reported. Figure 2.5 shows this configurations and simulated STM images [44] of molecular oxygen on the TiO₂ rutile (110) surface (images taken from references [44] and [54]).

In Figure 2.5(a) different adsorption geometries for the oxygen molecules on the TiO₂ rutile (110) surface are calculated. A to C show adsorption at a bridging oxygen vacancy, and D to I different configurations at five-fold coordinated titanium atoms. J and K present the calculated configurations for a dissociated oxygen molecule. The authors of reference [54] propose that the most favorable adsorption site on the surface is the one shown in C and that the dissociated configurations (J and K) are less favorable because of the high binding energy of a single oxygen atom to a perfect TiO₂ surface. As we will show below, molecular oxygen adsorbed in bridging oxygen vacancies and oxygen adatoms on the adjacent five-fold coordinated titanium atoms.

Figure 2.5(b) shows calculated Tersoff-Hamann images of the local density of states 4 Å above the surface [44]. These images suggest how STM images of the different configura-



Figure 2.5: Adorption position and simulated Tersoff Hamann plots of adsorbed molecular oxygen on a defective TiO_2 rutile (110) surface reported in the literature [44, 54].

tions look like.

In reference [31] another interesting fact is pointed out. The authors report that the dissociation of molecular oxygen can also take place on the troughs of five-fold coordinated titanium atoms at temperatures higher than 180 K, and that at higher temperature more oxygen molecules dissociate via this channel.

The adsorption and surface reactions of many other molecules have been studied, and the discussion of these is too much for this thesis to review. But one of them is important to be mentioned here: In reference [55] the adsorption behavior of carbon monoxide was analyzed. By studying low CO coverages on the TiO_2 rutile (110) surface the authors of this article investigated the preferential adsorption site of the molecule. In contrast to references [56, 57, 58], it was found out that the CO molecule adsorbs at a five-fold coordinated titanium atom on the surface, which is not directly adjacent to a bridging oxygen vacancy, but ont Ti_{5c} - Ti_{5c} distance away. Further they report that after adsorption the molecule may be negatively charged by backdonation of charge from the surface.

2.2 Anatase

The anatase polymorph is the other technically interesting form of TiO_2 . As mentioned in the beginning of this chapter, it consists of octahedra similar to the rutile. In anatase, however these are stacked in a different way, and they are distorted, which results in a different bandgap than in rutile crystals. When a TiO_2 crystal is grown, the preferential phase for nano-crystals is anatase, which is also known to be the photocatalytically more active one [59]. But if the size of the grown crystal exceeds a critical size of approximately $14\,\mathrm{nm}$, the anatase form becomes instable [60]. For larger sizes the rutile polymorph is the more stable one, and the anatase structure can be easily transformed into rutile. Depending on the amount and type of impurities, particle size, and the preparation history of a crystal, heating to temperatures in the range of 970 to 1270 K is sufficient to complete this transformation [61]. This makes the growth of large anatase single crystals challenging. Often naturally grown samples are used for studies. They are available more readily, but often contain different kinds and amounts of impurities. This makes most of them inappropriate for surface studies, but in rare cases, on these natural single crystals areas can be found, which are almost free from impurities and large enough for STM studies. Anatase single crystals are members of the tetragonal D_{4h}^1 -I4₁/amd space group [8]. The lattice parameters are $a = b = 0.3785 \,\mathrm{nm}$ and $c = 0.9514 \,\mathrm{mn}$ [62]. Surface energy calculations reported in reference [63] state that the anatase surface with the lowest surface energy is the (101), which is found in powder materials together with the (100)/(010). Usually anatase single crystals expose two crystal facets, the more reactive (001), and the dominating (101) surface [8, 64].

2.2.1 The Anatase (101) Surface

The TiO₂ anatase (101) surface can be viewed as a "sawtooth-like" surface consisting of step edges and "mini-terraces". The step edges of these mini terraces are formed by two-fold coordinated oxygen atoms. On the mini-terraces there are titanium atoms in two different configurations – five-fold and six-fold coordinated – and three-fold coordinated oxygen atoms (see Figure 2.6). Step edges on the surface are terminated by five-fold titanium atoms [65, 66].

Anatase crystals used in surface physics experiments are in general reduced (*i.e.*, oxygen deficient, as mentioned above). The extra titanium interstitial atoms and oxygen vacancies are providing excess electrons in Ti^{3+} states close to the bottom of the conduction band and are responsible for the n-type conductivity of most anatase samples [67].

In STM images, the TiO₂ anatase (101) surface appears different to the TiO₂ rutile (110) in atomically resolved images. It shows oval, bright spots in a row-like structure. The spots extend across the two-fold coordinated oxygen and five-fold titanium atoms on the mini-terraces (see figure 2.7).

Another difference to the rutile polymorph is the crystal symmetry. The TiO_2 anatase (101) surface has only a "pm" symmetry. This means that the crystal has no rotational symmetry. It has only one mirror axis only parallel to one crystallographic direction,



Figure 2.6: Ball and stick model of the TiO_2 anatase (101) surface



(a) $500 \times 500 \, nm^2$, 1.5 V, 0.27 nA, 78 K

Figure 2.7: STM images of the clean TiO₂ anatase (101) surface

but not the other one. In STM images like 2.7(a) trapezoidal islands are often visible. According to reference [66], the trapezoidal islands of the TiO₂ anatase (101) surface visible in 2.7(a) unambiguously define the directions on the surface. The parallel edges of the trapezoids are oriented along the [010] direction, while the non parallel edges are pointing in [$\bar{1}11$] or [11 $\bar{1}$] directions, which results from the formation energies of step edges that is related to the symmetry on the surface. Using this information, the [10 $\bar{1}$] direction (which

⁽b) The clean TiO_2 anatase (101) surface with an impurity marked by a red box. Imaging parameters: $10 \times 10 \text{ nm}^2$, 0.6 V, 0.5 nA, 79 K

is different from the $[\overline{1}01]$ direction) could be deduced from STM images.

The first STM images of the anatase surfaces have been recorded from natural samples (see e.g., reference [68]). However, natural crystals often contain many different impurities and the interpretation of the images was rather challenging. There were different defects or impurities visible in the STM images, but reference [8] reports that for a long time it was unclear, how a surface oxygen defect on an TiO₂ anatase (101) surface would appear in STM. The images presented in this work were recorded from a natural crystal that was almost free of impurities.

As mentioned above, one of the major differences between TiO_2 rutile and anatase is the density of surface oxygen vacancies in UHV. On rutile surfaces a certain number of them is always present, depending on the degree of reduction of the crystal (see section 2.1). There they are known to be the active centers for surface reactions [7, 8, 1, 69]. In contrast to rutile, DFT based calculations predicted that the stability of oxygen vacancies on the anatase crystals is higher in the subsurface region than directly on the surface [70, 19, 71].



Figure 2.8: DFT-based calculated energies of O_{vac} 's at different lattice positions. Red balls are oxygen atoms, blue ones titanium, yellow ones are oxygen vacancies and purple balls represent O_{3c} atoms on the edge of the sawtooth. V_{O1} , V_{O2} , V_{O3} , V_{O4} and V_{O5} mark the lattice position of the oxygen vacancies (yellow balls). The formation energies of the latter are shown in the energy diagram. Image taken from [71].

Defect site	Energy (eV)
V _{O1}	4.15(4.25)
V _{O2}	(5.40)
V _{O3}	(4.73)
V_{O4}	3.69(4.03)
V _{O5}	3.65

Table 2.1: Calculated formation energies in eV for different surface and subsurface oxygen vacancies on the TiO_2 anatase (101) surface. The energies were calculated using slabs containing 216 and 108 atoms. Values in brackets stem from the 108 atom slabs. Taken from reference [70].

The calculations predict that surface oxygen vacancies on the TiO_2 anatase (101) surface are less favorable than in the bulk, see references [19] and [70]. Reference [70] also presents the calculated formation energies (see Table 2.1 for oxygen vacancies at different positions shown in Figure 2.8. A different study (reference [71]) also reports that they found indications for subsurface vacancies and additionally published an STM image of surface defects on the TiO₂ anatase (101) surface. Reference [70] reports also the calculated pathway for a diffusion of a surface oxygen vacancy from the TiO₂ anatase (101) surface to the subsurface region, and it turned out that the barrier for subsurface diffusion is rather low (see table 2.2 taken from [19]).

Pathway	E_A (eV) direct pathway	E_A (eV) indirect pathway	Diffusion direction
$V_{O1} \rightarrow V_{O1'}$	2.65	2.65	[010]
$V_{O1} \to V_{O2} (1)$	1.52	0.47	[021]
$V_{O1} \to V_{O2} (2)$	1.34	0.30	$[66\overline{1}] + [0\overline{31}]$
$V_{O1} \to V_{O3} (1)$	1.34	0.78	$[66\overline{1}]$
$V_{O1} \to V_{O3} (2)$	1.52	0.96	$\left[0\overline{2}1 ight] + \left[031 ight]$
$V_{O2} \rightarrow V_{O3}$	0.30	0.78	[031]
$V_{O1} \rightarrow V_{O4}$	0.74	0.95	$[301] + [30\overline{1}]$
$V_{O2} \rightarrow V_{O4} (1)$	1.55	2.80	[201]
$V_{O2} \rightarrow V_{O4} (2)$	0.30	1.56	$[031] + [6\overline{6}1]$
$V_{O3} \rightarrow V_{O4}$	0.78	1.56	[661]

Table 2.2: DFT-GGA diffusion energy barriers along the pathways connecting the O_{vac} binding sites at or near the TiO₂ anatase (101) surface. The calculation was performed on a 71 atoms slab of TiO₂ anatase (101) (2 × 1). Taken from reference [19].

Nevertheless, there is no detailed experimental study about the oxygen vacancies on the TiO_2 anatase (101) surface. Reference [71] reports that electron bombardment can be used to create surface oxygen vacancies, but that these do not survive long in the residual gas, because they are covered with impurities from the residual gas. This thesis reports STM studies about the creation of the latter and their migration behavior as a function of temperature, which supports the proposed model of oxygen vacancies being more favorable in the bulk. The surface oxygen vacancies discussed in this work are not thermally formed, but created by ESD. This, according to references [72] and [73], is well suited for that purpose.

Although the subsurface oxygen vacancy migration was so far not proven, its influence on the surface chemistry of anatase is important for future technical applications. In the case of the TiO₂ anatase (101) surface, water adsorption was first studied in a combined study with TPD and XPS first (see reference [74]). The experiments revealed that water adsorbs molecularly on the TiO₂ anatase (101) facet. In the adsorbed state the oxygen atom of the water molecule is chemisorbed to the five-fold coordinated titanium atom. The hydrogenoxygen bond in the molecule stays intact and the hydrogen atoms are hydrogen bonded to the two-fold coordinated oxygen atoms on the edge of the sawtooth. DFT calculations (e.g., reference [63]) found the same result. References [75] and [76] further report that water is preferentially adsorbed on the TiO₂ anatase (101) surface in the vicinity of a subsurface defect. The authors of reference [75] report a DFT-based model supported by STM images of water adsorption on an TiO_2 anatase (101) surface.



(a) Water on the TiO_2 anatase (101) surface indicated by the red boxes. Imaging parameters: $2.5 \times 3 nm^2$, 1.2 V, 0.1 nA, 78 K



(b) Different appearance of an adsorbed water molecule on the TiO_2 anatase (101) surface. The red box shows an adsorbed water molecule, the blue one a black defect. Imaging parameters: $5 \times$ $5 nm^2$, 1 V, 0.35 nA, 79 K

Figure 2.9: STM images of water on the TiO_2 anatase (101) surface

In STM the adsorbed water molecules look rather large, because the electronic structure of the surface is altered in a large area (see Figure 2.9). The normal appearance of adsorbed water molecules on the TiO₂ anatase (101) surface is shown in Figure 2.9(a). In Figure 2.9(b) the adsorbed water looks different, which is due to the fact that its oxygen atom is chemisorbed on the five-fold titanium atom, while the hydrogen atoms interact with the two-fold coordinated surface oxygen atoms. The hydrogen bond is weak and therefore sometimes one of the hydrogen atoms is not bond to the surface, which result in different appearance in STM images (see also references [75] and [76]). Reference [75] additionally reports that water adsorbs more likely on reduced TiO₂ anatase (101) surfaces.

In section 2.1.1 it was already mentioned that on stoichiometric TiO₂ rutile (110) surfaces oxygen only physisorbs weakly (see also reference [46]). This is also true for the TiO₂ anatase (101) surface. However, if there are any excess electrons present, the adsorption is strongly enhanced. The adsorbed molecule becomes then negatively charged [52]. This excess charge can stem from various defects on the surface or in the bulk of the crystal. Oxygen vacancies are stable in the bulk as well as on the surface (at least at temperatures below 100 K), while interstitial titanium atoms are present in the bulk only. Another source for excess charge can be photo-excited electrons [51, 77]. Reference [76] reports that water as well as oxygen preferentially adsorbs on the undercoordinated five-fold coordinated titanium atoms on the TiO₂ anatase (101) surface. On a stoichiometric surface all five-fold coordinated titanium atoms are equal, but in the presence of e.g., titanium interstitial atoms or subsurface defects, their properties change [76]. Reference [67] reports that dissociative adsorption of oxygen is highly unfavorable and single oxygen adatoms on the TiO₂ anatase (101) surface are less stable than an oxygen molecule in the gas phase. When the oxygen molecule is adsorbed on the TiO₂ anatase (101) surface, it changes into a superoxide (O_2^-) state (see reference [78]), or into a peroxide state (O_2^{2-}) depending on the number of oxygen molecules dosed to the surface compared to the number of available subsurface defects [67]. However, an adsorbed oxygen molecule acts as an electron scavenger. It induces two π^* like states in the band gap, one somewhat below the conduction band minimum and the second above the valence band maximum.

Despite the amount of theoretical work, which provided many predictions for the TiO₂ anatase (101) surface and its properties, so far no detailed experimental study of surface defects exists on anatase. This thesis reports STM studies of the TiO₂ anatase (101) surface. In order to investigate surface oxygen vacancies, they were created by ESD and then analyzed with STM. Confirmation of surface oxygen vacancies on a clean TiO₂ anatase (101) surface created at 105 K is presented in detail. Also the thermal stability of the surface oxygen vacancies was investigated and it is shown that they are quite mobile at temperatures higher than approximately 250 K. Time-lapse STM images of surface defects at different on the TiO₂ anatase (101) surface also allowed to estimate migration energy barriers and to compare them to the work don by theorists. These time-lapse series of STM images also provide insights into the dynamics of the subsurface migration process. The results were published in reference [2].

In addition to this, the adsorption of gases on the clean surface and on the surface with oxygen vacancies was briefly studied.

Chapter 3

Experimental Techniques and Setups

3.1 Techniques

This chapter gives a short overview of the techniques used in the given work. Although the work is centered around STM measurements, additional methods were needed to prepare and characterize the sample's surface.

3.1.1 Scanning Tunneling Microscopy (STM)

In surface science STM is one of the most powerful, and often used technique. It was developed in the end of the last century by Binnig and Rohrer at the IBM research center in Rüschlikon. Its impact on the scientific community was enormous and resulted in a Nobel prize for the researchers in 1986. In contrast to surface diffraction methods, which are limited to periodic structures, an STM gives a direct, real space image of the sample's surface in atomic resolution. This means that also surface defects can be monitored. In STM one takes advantage of the quantum mechanical tunneling effect. A metallic tip is rastered a few Angströms above the sample, and due to the tunneling effect, electrons with insufficient energy to overcome the potential energy barrier between tip and sample, have a certain probability to travel through it. Mathematically this can be described using a one dimensional, rectangular potential barrier. If there is no tunneling voltage applied, resonant tunneling takes place between tip and sample states of the same energy without any preferential direction. But in most cases tip and sample have different work functions, and therefore even without a voltage an electrical field is present. A simple one-dimensional approach for the tunneling current is the following, using the time separated Schrödinger equation (3.1).

$$\left(\frac{\hbar^2}{2m}\nabla^2 + V\right)\psi = E\psi \tag{3.1}$$

m ... Electron mass V ... potential

The potential between tip and sample is approximated as a rectangular barrier of the height $\phi = V - E$. Inside the barrier, this results in decaying wave-functions as noted in equation (3.2).

$$\psi(z) \propto e^{-(\kappa z)}$$
 with $\kappa = \sqrt{\frac{2m\phi}{\hbar^2}}$ (3.2)

The probability is proportional to $|\psi|^2$ and decays exponentially with $e^{-2\kappa z}$. Assuming the width of the barrier is d, the transmission (T) and hence the tunneling current (I_t) can be approximated via the following equation (3.3).

$$I_t \propto T \propto |\psi(d)|^2 \propto e^{(-2\kappa d)}$$
(3.3)

The exponential decay causes a large change of the tunneling current when there is a small change in the barrier width (distance between tip and sample). If the current is kept constant within a few percent, a resolution in z of 1 pm can be achieved.

For a mathematically more detailed description of the tunneling more parameters must be taken into account. The most important ones are the Densities of states (DOS) of tip and sample, different Fermi levels, the three-dimensional geometry and the interaction of tip and sample at low distances between the two latter. A simple, but effective approximation for I_t is the Tersoff-Hamann model [79, 80], which is based on the Bardeen approach [81]. The model assumes a spherical tip of a certain radius. Further, it only takes into account s-waves and the wave functions of the sample are characterized by plane Bloch waves. In this simple model of constant density of states (DOS), the tip follows the sample's topography, but when the local density of states (LDOS) is more complex, it depends on both, the sample's electronic structure and the topography (as e.g., in TiO₂ rutile (110)). In a laboratory environment, an STM can be used in three main operating modes:

- Constant Current Mode (CCM): In this mode the tunneling current (I_t) is kept constant by a feedback loop and the adjusting signal of the z piezo to keep the current constant is taken to build the image. It is the most-commonly used mode, and is also applied in this thesis work.
- Constant Height Mode (CHM): Here the STM tip is rastered over the surface, and the tunneling current (I_t) is recorded. The speed of the image recording is much higher in this mode than in the previous, but it requires large and flat terraces on the sample, because the danger of crashing the tip is very high. But, if the sample's surface is really flat and the terraces are large enough, faster scanning than in CCM mode is possible, and the danger of crashing the tip in case I_t is zero is lower than in CCM mode.

• Scanning Tunneling Spectroscopy (STS): In STS the feedback loop is only used for setting the initial height. Then it is switched off and the gap voltage (U_g) is varied, while the tunneling current (I_t) is recorded. This is used to study electronic states, which are localized on the surface, or to investigate the band gap of semiconductors.

Practically the STM is operated by piezo actuators. In many systems, there are three "coarse piezos" to define the position of the tip relatively to the sample, and a scanning tube. The later is usually comprised of a piezo tube, which can be elongated or contracted to define the tunneling gap. On the outer diameter of this tube, four electrodes are present to enable the rastering in two directions.

3.1.2 Auger Electron Spectroscopy (AES)

For surface analysis, AES is a very important and (relatively) easily available method, which is non-destructive for metals. In case of oxides this is not true because of electron stimulated desorption (ESD) (see below). When a sample is irradiated by an electron beam $(1 \dots 10 \text{ keV})$ [82], electrons from an inner shell can be emitted. As a result of this primary collision, an electron hole is produced, and this hole is filled without emitting irradiation by an electron of usually the same atom coming from an outer shell [83, 84]. This energy is transfered to a third electron (the "Auger" electron), which is then emitted from the sample. The Auger effect is most effective for electrons, which populate the same shell, because of Coulomb interaction. In a first-order approximation the energy of the emitted electron fulfills equation (3.4), and is independent of the energy of the primary electron. Here, no correlation or shake-up effects are taken into account. The sketch in Figure 3.1 shows a $\text{KL}_{II}\text{L}_{I}$ process.



Figure 3.1: Sketch of an Auger process

$$E_{kin} = E_K - (E_{L_{II}} + E_{L_I}) - \phi \tag{3.4}$$

- E_{kin} ... Kinetic energy of the Auger electron
- E_K ... Binding energy of the emitted core level electron
- $E_{L_{II}}$... Binding energy of the hole-filling electron
- E_{L_I} ... Binding energy of the Auger electron
- E_F ... Fermi level
- $E_V \quad \dots \quad \text{Vacuum level}$
- ϕ ... Work Function

Binding energies are usually counted positive with respect to the Fermi level, which is set to zero. The energies of Auger electrons are characteristic for the emitting atom, and the depth of information is mainly dependent on their inelastic mean free path (IMFP; minimum: ≈ 4 to 10 Å for energies between 10 and 100 eV) in the crystal, which can be seen from the universal curve. In general, Auger signals are rather small and thus normally the recorded spectrum is differentiated to subtract the background of inelastically backscattered primary electrons. The minimum of this differentiated signal is assigned to the Auger energy. This enhances the visibility of the characteristic Auger peaks, and by measuring the distance between the minimum and maximum of the observed peak (APPH: Auger Peak to Peak Height) one can determine the intensity of the peak with respect to a reference peak.

3.1.3 Low Energy Electron Diffraction (LEED)

Diffraction works best if the wavelength of the diffracted mono-energetic electrons is in the range of the distance between scattering obstacles [82]. To determine the wavelength of the electrons, the de Broglie equation (3.5) is used.

$$\lambda = \frac{h}{\sqrt{2mE}} \approx \sqrt{\frac{150}{E_{kin}}} \tag{3.5}$$

- λ ... Wavelength of the electron in Å
- h ... Planck's constant
- m ... Electron Mass
- E ... Energy

 E_{kin} ... Kinetic energy of the electron in eV

Electrons with energies between 50 and 500 eV have therefore wavelengths between 1.7 and 0.5 Å. This is of the same order of magnitude as typical atomic crystal lattice distances. The mean free path of these electrons can be determined from the "universal curve", as approximately 4 to 10 Å. Therefore this technique is highly surface sensitive.

The incident electrons are backscattered at the sample's surface. The wave functions of diffracted and incident electrons superpose and form, depending on the wavelength of the incident electrons, diffraction maxima and minima. The resulting diffraction pattern is an image of the reciprocal lattice of the studied sample. In a one-dimensional approximation, the maxima can be found according to the following equation:

$$a\,\sin\,\phi = n\,\lambda\tag{3.6}$$

a	 Lattice constant
ϕ	 Angle between surface normal and diffracted electrons
n	 Order of the maximum
λ	 Wavelength of the incident electrons

To gain information about the maxima in two dimensions, the lattice constant *a* is replaced by the row distance d_{hk} in direction of the Miller indices (hk). Thus follows that for primary electrons with a kinetic energy E_{kin} and perpendicular incidence to the surface, diffraction maxima can be found according to the following equation (3.7)

$$\sin \phi = \frac{n}{d_{hk}} \sqrt{\frac{150}{E_{kin}}}.$$
(3.7)

 ϕ ... Angle between surface normal and diffracted electrons

n ... Order of the Maximum

 d_{hk} ... distance between rows of atoms in Å

 E_{kin} ... Kinetic energy of the electron in eV

For three-dimensional lattices, the reciprocal lattice is also three-dimensional. Thus, when diffraction is taking place at a surface, the third component is missing and therefore the reciprocal lattice of a surface is not a point lattice, but consisting of rods perpendicular to the surface (crystal truncation rods). Thus follows that the Ewald sphere always cuts rods of the reciprocal lattice and a diffraction pattern is formed for every energy.

Experimentally the backscattered electrons are detected on a screen, which is at a positive bias of several thousand Volt. In most setups, electrons have to pass two grids before hitting the screen, the first one at ground, the second at variable negative voltage to prevent inelastically scattered electrons from reaching the screen. The screen image is then recorded by an external camera for further processing.

3.1.4 Low-Energy Ion Scattering (LEIS)

When ions in the energy range between several hundreds up to some thousands of electron volt hit a solid, they are scattered by the surface atoms via two-particle collisions. The energy of the recoil ions is related to the atomic mass of the sample atom according to equation (3.8)

$$E_{1} = E_{0} \left[\frac{M_{1}}{(M_{1} + M_{2})} \left(\cos\vartheta \pm \sqrt{\frac{M_{2}^{2}}{M_{1}^{2}} - \sin^{2}\vartheta} \right) \right]^{2}.$$
 (3.8)

- E_0 ... Energy of the incident primary ion
- E_1 ... Energy of the scattered primary ion
- M_1 ... Mass of the incident primary ion
- M_2 ... Mass of the surface atom

 ϑ ... Scattering Angle of the primary ion

In order not to change the investigated surface too much by sputtering, intermixing and implementation of projectile ions, noble gas ions (*i.e.*, He^+) are used. The high neutralization probability of rare gas ions (especially helium), which enter a solid, makes this technique highly surface sensitive, and allows us to get qualitative information about the topmost atomic layer.

In this work, 1 keV He⁺ ions and a hemispherical energy analyzer have been used.

3.1.5 X-Ray Photoelectron Spectroscopy (XPS)

In XPS, core electrons from the sample are excited with x-rays. If the x-ray energy is sufficient to excite the electrons above the vacuum level, they can leave the sample. In the "frozen orbital approximation" the energy levels of the remaining electrons are unaltered, and the following equation (3.9) is valid:

$$h\nu = E_B + \phi + E_{kin} \tag{3.9}$$

 small

 $\begin{array}{cccc} h & \dots & \text{Planck's constant} \\ \nu & \dots & \text{Frequency of the x-rays} \\ E_B & \dots & \text{Binding energy of the electron} \\ \phi & \dots & \text{Work function} \\ E_{kin} & \dots & \text{Kinetic energy of the emitted electron} \end{array}$

The binding energy of the electron depends on its chemical surroundings. Therefore XPS is not only sensitive to different elements, but also to the oxidation state of the atom, from which the electron was emitted.

In addition to this sensitivity to the oxidation state, advantages of XPS are also that it can be applied to isolators, and that the x-rays cause hardly any damage to the sample. In XPS experiments, some issues are important to consider: When the spectrum is recorded without a monochromator, satellite maxima can appear, which stem from the same element, but are excited from a different x-ray frequency. Another reason for satellite lines are the "electron shake up/off" effects. These appear, when excited states result from the core hole creation, or electrons are emitted, respectively. Also Auger electrons are observed, which can be identified by switching to a different anode material. This changes the frequency of the x-rays and therefore all XPS peaks are shifted. The Auger lines are at the same binding energies in spectra recorded with different x-rays.

3.2 Experimental Setups

The systems, which were used for carrying out the experiments described in this work are adapted commercial Ultra High Vacuum (UHV)-systems for surface analytics. The acronym UHV stands for base pressures in the range of 10^{-7} to 10^{-13} mbar. This is an essential condition for surface investigations, because it slows down the adsorption of gas particles from the surroundings and conserves the same conditions on the sample's surface for several hours. This chapter gives a short overview over the different experimental setups used to investigate the crystals.

3.2.1 The Low Temperature Scanning Tunneling Microscope (LT-STM)

The LT-STM consists of two UHV chambers, which can be separated by a valve. One chamber is dedicated to sample preparation and some analysis techniques, while the second is only used for Scanning Tunneling Microscopy (STM) analysis (See Figure 3.2). The UHV in both chambers is created by a rotary vane pre-pump and a turbo-molecular pump connected to the preparation chamber. In addition, both chambers are evacuated by two ion getter and titanium sublimation pumps. Because it is absolutely necessary to decouple the UHV system from vibrations (e.g., vibrations of the building) during STM measurements, the whole system can be pneumatically lifted and then floats on air cushions. The preparation chamber is equipped with the instruments to perform LEED and AES. Further there are an ion gun and an electron-beam heating station (up to 1200 K) for sample preparation, a quadrupole mass spectrometer for gas composition investigation, an electron gun, and several high precision leak values for gas dosing. The system is also equipped with a manipulator to transfer the samples from one chamber to the other and to place the sample at the various positions for different preparation and analysis techniques. The head of the manipulator is thermally isolated from the rest and equipped with a resistive heating stage, which can also achieve temperatures up to approximately 700 K. If desired, it is also possible to cool the head with liquid nitrogen to approximately 100 K for low-temperature preparation. In order to bring the sample for a short time to a specified temperature outside the LT-STM, the manipulator was either resistively heated, or cooled by liquid nitrogen. The analysis chamber is equipped with a high precision leak valve and with a customized,



Figure 3.2: Schematic view of the LT-STM system. Taken from reference [85]

commercial Omicron LT-STM. It consists of the STM, shielded by two gold-plated walls cooled by cryostats. Most of the time both cryostats are filled with liquid nitrogen (lN_2) , which fixes the temperature of the STM at 78 K. For even lower temperatures the inner cryostat is filled with liquid helium (lHe) and the outer one with liquid nitrogen to shield the inner one from thermal radiation from the environment and to keep the liquid helium consumption as low as possible. In order to measure at temperatures in between the five easy achievable points (5, 10, 17, 78 and 300 K) two different techniques were applied. First via resistive heating of the cold STM and stabilizing it via the heating current at desired temperatures. The second possibility to access the intermediate temperature range is to cool the STM from ambient temperature by filling the outer cryostat with liquid nitrogen. This results in a very slow cooling rate (with an almost constant temperature for several hours), and the temperature is variable by choosing different refilling intervals and amounts. In the interval between 17 and 300 K the best way to achieve a certain temperature and to stabilize it is to employ both methods simultaneously. In section 4.3.1 a temperature of 17K was achieved by cooling the inner cryostat with liquid helium and the outer one with liquid nitrogen. Normally this technique would cool the STM to 5K, but in this case both cryostat doors were kept open and the temperature was stabilized at 17K.

On each chamber there is also a special flange, which can hold an optical lens system to irradiate the samples with a laser or other optical instruments from the outside. The used laser is a "Quanta Ray PRO 290" series Nd:YAG type with a wavelength of 1064 nm with
the possibility to use a harmonic generator (KD*P crystal), which doubles or triples the emitted frequency. The wavelengths used in this work were 532 and 355 nm, respectively.

3.2.2 The SPECS System

This setup is also a two chamber system. In the preparation chamber, a SPECS mini MBE (Molecular Beam Epitaxy) system, all the sample preparation is carried out, while in the analysis chamber primarily the analysis is done. The preparation chamber is equipped with several high precision leak valves, a sputter gun, an oxygen plasma source, a quartz crystal micro balance, a setup for Reflection High Energy Electron Diffraction (RHEED) analysis, and a heating stage. Samples are inserted into the preparation chamber via a load lock and moved inside the system from one chamber to the other by magnetically coupled transfer rods. In the analysis chamber there is a SPECS Aarhus 150 STM, another sample heating stage, an Omicron x-ray gun, a sputter gun, a LEED instrument and a hemispherical energy analyzer. The entrance and exit slits and the iris of the analyzer are adjustable to set the acceptance area when doing XPS, which enabled to examine the rather small anatase sample.

3.2.3 The PINUP System

This system consists of one large single UHV chamber with a base pressure below 10^{-10} mbar. The chamber has three areas: In the bottom, there is a homebuilt system for Surface Magneto Optical Kerr Effect (SMOKE) analysis. The central section is used for AES and LEED measurements, while the upper part is used for sample preparation and Ion Scattering Spectroscopy. There are two ion sources – one is used for sample preparation (sputtering), and the other one together with the hemispherical analyzer for LEIS measurements.

Chapter 4 The Rutile (110) Surface

The results on the TiO₂ rutile (110) surface reported in this work were obtained by STM studies at low temperatures on two different TiO₂ rutile (110) crystals. They were bought from CrysTec and MTI Coorporation, respectively. They were both mounted on a tantalum sample plate using tantalum clamps. A small sheet of gold foil was placed between the sample and the sample plate in order to improve the thermal contact. No significant difference of the samples was detectable, so there will be no special notation about the crystals in this chapter.

4.1 Crystal Preparation

The crystal preparation was done in the preparation chamber of the LT-STM (see section 3.2). For an ordered, flat surface the sample was sputtered for ten minutes using argon ions (Ar⁺) with an energy of 2000 eV. The sputtering was done using a rasterable sputter gun with a fluence of 4×10^{16} Ar⁺ ions per cm². To direct the ion beam onto the sample, the sample current with respect to the signal from the ion gun's raster generator was monitored. Via this image it was possible to adjust the beam width to the width of the sample. After sputtering, the crystal was annealed in UHV for ten minutes via an electron beam heating stage at temperatures between 923 and 1123 K. The annealing temperature was readjusted several times, because after tens of preparation cycles, the tantalum clamps sometimes got a little looser and therefore the temperature setpoint had to be adjusted to obtain the same temperature of the sample.

If the crystal had already been prepared before, two sputtering/annealing cycles were sufficient to obtain a clean TiO_2 rutile (110) surface with reasonable terrace sizes. In chapter 2.1 it was mentioned that sputtering and annealing TiO_2 crystals leads to a reduction of the crystal and the formation of bridging oxygen vacancies on the surface. The density of the latter in the experiments reported here was approximately 0.17 ML (monolayer).

4.2 Crystal Characterization

After the first preparation cycles an AES spectrum was recorded to test the preparation and if there were any impurities present. This quick measurement gives evidence about any kind of impurities in the topmost layers of the sample (see section 3.1.2). The crystal was investigated with electrons of a primary energy of 3 keV and the differentiated intensity plotted *versus* the electron energy. Figure 4.1 shows a typical spectrum recorded from a clean TiO₂ rutile (110) crystal.



Figure 4.1: Differentiated Auger spectrum of a clean sputtered and annealed TiO_2 rutile (110) sample

It shows peaks assigned to titanium and oxygen, as expected. At an Auger electron energy of 218 eV [86] there is another peak visible. This was assigned to argon, of which small amounts likely were incorporated into the sample during sputtering. The spectrum was also analyzed for peaks of commonly known impurities of TiO₂, in particular potassium, calcium, aluminum and magnesium. But even the strongest Auger peaks of the mentioned impurities were absent in the spectrum, which indicated that the surface was clean.

For STM studies done in the LT-STM (see section 3.2.1), tunneling parameters for the rutile crystals were a current in the range from 0.004 to 0.4 nA and a positive sample bias voltage between 1.3 and 2.4 V. In the LT-STM the images were recorded at two different, easily reproducible, and stable temperatures: 17 and 78 K. Tunneling at 5 K, which is the lowest working temperature of the LT-STM, was impossible, because the conductivity of the sample at this temperature was insufficient for stable tunneling. So the whole STM was heated to 17 K, where normal STM operation could be established.

In Figure 4.2 a typical image of a clean TiO_2 rutile (110) surface is shown. Bridging oxygen vacancies are easy to recognize as the bright connections between bright titanium rows (for



Figure 4.2: O_{vac} defects on the TiO₂ rutile (110) surface. Imaging parameters: $10 \times 10 \text{ nm}^2$; 1.4 V, 0.45 nA, 16 K

more details see section 2.1). Titanium interstitial atoms are located in the bulk of the crystal and therefore invisible for the STM.

4.2.1 CO Adsorption

In order to perform the oxygen adsorption studies on the TiO_2 rutile (110) surface, it was necessary to gather knowledge about the most common impurities in the used residual gas. During the oxygen dosing, oxygen replaces CO at the inner chamber walls, which results in reasonable amounts of CO in the residual gas. Therefore a series of CO adsorption experiments was done to study the adsorption of this molecule on the clean surface. The goal of this experiment was to find out the adsorption position and the appearance in STM of CO in order not to misinterpret later-recorded images where the oxygen adsorption was studied.

Figure 4.3(b) shows a very low coverage with CO (red box), some bridging oxygen vacancies (blue box) and terminal hydroxyl groups (green box). The STM image in Figure 4.3(b) shows a magnification of the image in Figure 4.3(a). According to reference [55], the CO molecule preferentially adsorbs at the next nearest neighboring five-fold titanium atom to a bridging oxygen vacancy and not in the bridging oxygen vacancy itself. This could be confirmed by the STM image in Figure 4.3(b).

When the dose of CO is increased, the CO molecules also occupy five-fold coordinated titanium atoms, which are not adjacent to a bridging oxygen vacancy. The STM image in Figure 4.4 shows a TiO₂ rutile (110) surface, which was exposed to 15 L of CO.



 (a) CO adsorbed on a clean TiO₂ rutile (110) surface. Imaging parameters: 40 × 40 nm², 1.4 V, 0.3 nA, 78 K



(b) Adsorbed CO on the TiO_2 rutile (110) surface. Red box: CO molecule; blue box: $O_{\rm vac}$; green box: OH group at a bridging oxygen position. Imaging parameters: $10 \times 10 \text{ nm}^2$, 1.3 V, 0.6 nA, 78 K

Figure 4.3: STM images of a sputtered and annealed TiO_2 rutile (110) surface with adsorbed CO

4.3 Results and Discussion

4.3.1 Oxygen Adsorption at 17 K

To study the phenomena taking place on the TiO_2 rutile (110) surface upon oxygen adsorption, the sample was exposed to molecular oxygen (see section 4.1). What happens at room temperature is already well known (see section 2.1). But how it works at 100 K is still unclear.

Oxygen dosing to the crystal was done at a pressure of 1×10^{-9} mbar for one minute. The dose was 0.05 L of oxygen for the experimental results shown below.

After dosing, the same area on the sample was scanned with STM several times using the same tunneling parameters. STM images of the oxygen-exposed surface are shown in Figure 4.5.

After a dose of 0.045 L (1 Langmuir (L) corresponds to $10^{-6} \text{ torr} \times \text{seconds}$) of oxygen, on the TiO₂ rutile (110) surface bridging oxygen vacancies and bright, round spots were identified. The bright spots are located on the five-fold titanium rows and are identified as oxygen adatoms (see also reference [87]). But if the image is compared to a clean TiO₂ rutile (110) surface, the numbers do not add up. In images recorded after preparation of the clean surface of a slightly reduced sample (*e.g.*, Figure 4.2) on a comparable area 120 \pm 20 bridging oxygen vacancies are visible (0.17 ML). In the image shown in Figure 4.5(a)



Figure 4.4: STM image of the TiO₂ rutile (110) surface with high coverage of CO; $40 \times 40 \text{ nm}^2$, 1.3 V, 0.27 nA, 78 K

only 58 vacancies are counted. From earlier studies (e.g., reference [88]) it is known that molecular oxygen is chemisorbed on the TiO_2 rutile (110) surface at temperatures lower than 120 K. The adsorbed molecules can then dissociate at bridging oxygen vacancies. The vacancy is healed and the excess oxygen atom forms an adatom on an adjacent five-fold titanium atom. Therefore also the oxygen adatoms were considered and 27 adatoms were counted. In total 85 defects and adsorbates were found, which is clearly less than the defect count of 120 on a clean surface. Further inspection of the STM image in Figure 4.5(a) reveals many horizontal streaks and some only partially-visible oxygen adatoms. Apparently this is due to interaction of the STM tip with the sample, which results in the formation of additional adatoms during scanning. Indeed the number of adatoms increases with the number of scans done at the same position on the surface. By direct comparison of the first image (Figure 4.5(a)) recorded in a series of STM images to an image recorded two images later (Figure 4.5(b)), two remarkable differences are revealed. First, the number of oxygen adatoms on the later recorded image (Figure 4.5(b)) is higher by a number of 29. These "appearing" adatoms are marked with small red circles in the difference image 4.5(c). After a more detailed analysis of the images, a second difference was found. On the STM image in Figure 4.5(a) positions could be found, where the contrast along the bridging oxygen rows is slightly brighter than normal, and also smeared out along the rows (see orange box in Figure 4.5(a)). It can be definitely excluded that this feature is a bridging oxygen vacancy, which would appear much brighter and more localized in the image. Due to the fact that the titanium rows in the neighboring surroundings show no change in contrast, this is assigned to a highly localized feature, affecting only the bridging oxygen rows. These features could not be found in Figure 4.5(b). For a direct comparison



(a) Features on the surface are indicated by colored boxes. Red: bean-shaped O_{ad} 's, white: two independently formed O_{ad} 's blue: O_{ad} on a Ti_{5c} atom, orange: adsorbed oxygen molecule in an O_{vac} , green: O_{vac} .



 (b) STM image of the same area as shown in 4.5(a) after scanning it several times.



(c) Difference image of the images 4.5(a) and 4.5(b). The bright spots indicate tip-induced oxygen adatoms that appear in image 4.5(b).

Figure 4.5: Reduced TiO₂ rutile (110) surface after exposure to $0.045 L O_2$ at $\approx 100 K$. Imaging parameters: $37 \times 28 nm^2$, 1.8 V, 0.05 nA, 17 K

the difference between a bridging oxygen vacancy and the faint contrast feature is shown in Figure 4.6(a). Figure 4.6(b) shows a line profile, which was recorded along the red line in Figure 4.6(a). It presents the height of the faint contrast feature relative to the bridging oxygen rows. Compared to a bridging oxygen vacancy, which is typically 55 pm higher than the bridging oxygen rows, this is only 25 pm higher than the row.

In the STM images in Figure 4.5 even more details could be discovered. After oxygen exposure there are often pairs of oxygen adatoms visible, which sit on adjacent titanium rows. But these pairs do not all look the same. Two different forms could be identified, which are demonstrated in the STM images in Figure 4.7. These two forms are also marked in Figure 4.5(a) with red and white boxes, respectively.

The origin of these adatom pair from an oxygen molecule, which was dissociated on a



(a) Creation of an oxygen adatom on a Ti_{5c} atom, which is partially visible in the upper part of the red circle. Imaging parameters: $8 \times 6 \text{ nm}^2$, 1.8 V, 0.03 nA, 17 K



(b) Lineprofile over the faint contrast feature in Figure 4.6 (along the red line)

(c) Lineprofile over the bridging oxygen vacancy in Figure 4.6 (along the blue line)

Figure 4.6: Detailed view of a faint contrast feature (red circle in Figure 4.6(a)) on a $O_{\rm br}$ row and height profiles over a bridging oxygen vacancy (blue line), and the faint contrast feature (red line). Note the difference in apparent height between an $O_{\rm vac}$ and the faint contrast feature. Additionally the formation of an oxygen adatom is visible in the upper region of the red circle, where the contrast is brighter than below.

titanium interstitial atom at 120 K as reported in reference [88] can be excluded: The dissociation as reported in this reference [88] results in an adatom pair with the two oxygen adatoms sitting on the same titanium row, while the adatom pairs in Figure 4.7 are occu-



(a) Imaging parameters: $10 \times 8 nm^2$, 1.8 V, 0.05 nA, 17 K



(b) Imaging parameters: $10 \times 8 nm^2$, 1.8 V, 0.05 nA, 17 K

Figure 4.7: Magnification of the two different forms of adsorbed oxygen adatom pairs on adjacent titanium rows

pying positions on adjacent titanium rows. The shape of the adatomi in the pair shown in Figure 4.7(a) is perfectly circular with slightly enhanced contrast on the bridging oxygen row in between the two adatoms. In contrast, the adatoms in Figure 4.7(b) show an oval, almost "bean-like" shape, and in addition to this the contrast of the space between them on the bridging oxygen row is dark.

Another interesting phenomenon was observed in series of time-lapse STM images recorded at 17K after oxygen dosing at 100K. Sometimes an adatom pair as shown in the STM image in Figure 4.7(b) was created by the STM tip and could be identified in several STM images. After some minutes it then suddenly "decayed" into a single adatom on one of the neighboring titanium rows, see Figure 4.8.

A deeper analysis of the time-lapse STM images led us to propose the following mechanism: The tip can interact with one of the smeared-out faint contrast regions on the bridging oxygen rows. This interaction results in the formation of a bean-shaped adatom pair, which can then again interact with the tip and in the last step lead to an oxygen adatom on an adjacent titanium row. This phenomenon is shown in the STM images in Figure 4.8, together with ball and stick models to clarify the process.

In all STM images presented here the slow scanning direction is bottom-to-top, and therefore it is obvious that the tip is creating the adatom, which can only be seen partially in image 4.8(a). It is also concluded that the freshly-created adatom has its origin from a smeared-out faint contrast feature on the bridging oxygen rows, which is also visible in the center of Figure 4.8(a). The following image 4.8(b) shows that the smeared-out feature on the bridging oxygen row has disappeared, while on the titanium rows directly adjacent to its position two oxygen adatoms have appeared, which exhibit the above described bean-shape. Scanning the area again leads to another tip – sample interaction, which was





(a) Imaging parameters: 1.8 V, 0.03 nA, 17K





(b) Imaging parameters: 1.8 V, 0.03 nA, 17 K



(c) Imaging parameters: 1.8 V, 0.03 nA, 17K

(d) Imaging parameters: 1.8 V, 0.03 nA, 17 K

Figure 4.8: Time-lapse STM images showing the creation and destruction of an adatom pair on the TiO_2 rutile (110) surface. In addition to this there is a ball and stick model added to all STM images to present the mechanism.

directly imaged in image 4.8(c). The bottom right adatom of the bean-shaped pair is still intact, while the upper left disappears during the scan. A small part of the former adatom is still visible in image 4.8(c). The last image of this series is shown in Figure 4.8(d). It presents the stable, final state of this whole process. The leftover adatom does not show the bean-like shape any more, but looks circular and symmetric. An inspection of the whole image recorded revealed that there was no difference between this adatom and other oxygen adatoms on the surface, which have already been observed in the first image. The STM images were all recorded at 17 K. Although at this temperature adatom mobility could be excluded, the surroundings of the spot, where the dissociation took place was inspected. However, no movement or disappearing of adatoms could be detected.

The tip-induced creation of oxygen adatoms is strongly correlated with the tunneling conditions. When scanning the surface with "mild" conditions (e.g., voltages of 1.5 V and currents below 0.06 nA at 17 K), there are hardly any oxygen adatoms created. In contrast, imaging the surface with "harsh" tunneling conditions (e.g., 2.4 V and 0.3 nA) leads to tip-induced dissociation of all oxygen molecules, which have been adsorbed on the TiO₂ rutile (110) surface, within one single scan (see STM images in Figure 4.9).



(a) Imaging parameters: $40 \times 40 \text{ nm}^2$, 1.3 V, (b) Imaging parameters: $40 \times 40 \text{ nm}^2$, 1.3 V, 0.05 nA, 17 K

Figure 4.9: The first and last image of a series of STM images. Image 4.9(a) shows the first scan of the surface, where most of the O_2 molecules are still intact, while image 4.9(b) shows the last image of the series after scanning it under "harsh" conditions (2.4 V, 0.3 nA)

The red bars in Figure 4.9 indicate the number count of bridging oxygen vacancies prior to dosing oxygen and oxygen adatoms visible in the STM images after dosing and scanning with "mild" and "harsh" conditions (see Figures 4.9(a) and 4.9(b)), respectively. It is obvious that after scanning at "harsh" conditions the number of bridging oxygen vacancies before dosing oxygen and the numbers of bridging oxygen vacancies and oxygen adatoms after "harsh" scanning are equal within statistical variance.

It could also be observed that the tip-sample interaction, which induces the dissociation of adsorbed oxygen molecules, is rather localized. In order to study this in more detail a series of STM images was recorded, in which the tunneling parameters were changed rapidly. After scanning the lower half of the image in Figure 4.10 with "harsh" conditions, the tunneling voltage and current were instantly switched to "mild" conditions and the rest of the image was recorded using the latter parameters. The red line in the STM image in Figure 4.10(a) indicates the line where the parameters were changed. There is an obvious difference in the number of adatoms in both halves of Figure 4.10(a).

In the lower half, there are more oxygen adatoms visible than in the upper one. To check



(a) Imaging parameters: $10 \times 10 \text{ nm}^2$, 1.8 V, 0.06 nA, 17 K



(b) Imaging parameters: $10 \times 10 \text{ nm}^2$, 2.4 V, 0.3 nA, 17 K

Figure 4.10: STM images showing that the dissociation of O_2 due to the STM tip is highly localized. The lower part of the STM image in Figure 4.10(a) was recorded with "harsh" tunneling conditions, while the part above the red line was recorded with mild imaging conditions. There are more oxygen adatoms visible in the lower part of the image 4.10(a) than in the upper one. In order to check that this is not only local fluctuation of the adatom density, the whole image was scanned at harsh conditions. The result is shown in Figure 4.10(b). It shows the same spot on the surface as image 4.10(a), but in the top half there are more oxygen adatoms visible than in image 4.10(a). The red line marks the position of the STM tip in image 4.10(a) where the scanning parameters have been changed.

whether the adatoms were really created by scanning with "harsh" tunneling conditions, the whole image was scanned again with "harsh" conditions (see Figure 4.10(b)). After that the numbers of adatoms both in the lower and in the upper half of the image are the same. This shows that many adsorbed oxygen molecules were still intact in the upper half of Figure 4.10(a) after scanning with "mild" conditions. Only after scanning with "harsh" parameters, they were dissociated, and as a direct result of the tip – sample interaction oxygen adatoms were created.

4.3.2 Oxygen Adsorption at 78 K

The STM images presented in the last paragraphs have all been recorded at 17 K. This marks the lowest temperature, at which stable STM tunneling conditions on the TiO₂ rutile (110) crystal could be established.

Figure 4.11 shows STM images of the same experiment as described above, but the STM images were recorded at 78 instead if 17 K.



(a) Blue box: rare case of the occurrence of a "bean-shaped" adatom pair at 78 K. Red box: spot, where an O_2 molecule is adsorbed in a O_{vac} and in image 4.11(b) an adatom is appeared. Imaging parameters: $15 \times 15 \text{ nm}^2$, 1.5 V, 0.1 nA, 78 K



(b) Consecutive scan of the same area as shown in Figure 4.11(a). Imaging parameters: $15 \times 15 \text{ nm}^2$, 1.5 V, 0.1 nA, 78 K

Figure 4.11: STM images recorded at 78 K. Note that they also show O_{vac} 's and O_{ad} 's, which could be observed at a sample temperature of 17 K, but that the bean-shaped adatom pairs could only be observed in rare cases. At 17 K in almost every recorded STM image one or two of these bean-shaped adatom pairs are visible. Further the characteristic streaks for the O_2 dissociation are visible in the image 4.11(a).

Similar to Figure 4.9, in Figure 4.11 the first (Figure 4.11(a)) and last (4.11(b)) image of a series of STM images are presented. First the surface was scanned using "mild" tunneling parameters in order not to dissociate the adsorbed oxygen molecules on the surface. In the STM image shown in Figure 4.11(a) the same features could be identified as in the STM images recorded at 17K: bridging oxygen vacancies, as well as adsorbed oxygen molecules, and oxygen adatoms are visible. But the main differences between the images recorded at 17K and 78K are that there are very few "bean-shaped" adatom pairs visible and that there are more adatoms visible in the first scan. Further, in Figure 4.11(a) there are many streaks visible, which mark spots, where a tip-sample interaction occurs. This results in the dissociation of an oxygen molecule and the formation of an oxygen adatom pair. The STM image in Figure 4.11(b) was recorded after scanning the surface with "harsh" conditions. The difference is not as big difference as in a similar experiment carried out at 17K, compare Figures 4.11 and 4.5. Thus, the majority of the oxygen adatoms have already been formed in the first scan. In this case in image 4.11(a) 53 adatoms (including

also half visible ones, which were about to be created by the tip) were counted, while in image 4.11(b) 59 adatoms could be identified.

4.3.3 Influence of STM Tunneling on Oxygen Adatom Creation

In order to reveal the physical reason for the tip-induced dissociation the tunneling current was varied in the range of more than one order of magnitude (*i.e.*, 0.004 to 0.05 nA), while all other parameters were kept constant. The tunneling voltage was fixed at 1.3 V, which turned out to be the lowest voltage, which could grant stable, reproducible images while reducing the influence of the electrical field of the STM tip as much as possible. A large scatter of the adatom creation range could be found (0.0077 ML per scan with a standard deviation of 0.0035 ML per scan), and the creation rate showed no significant correlation with the tunneling current, see Figure 4.12.

A similar series of experiments, with the tunneling voltage being varied could not be performed. On the one hand, clear STM images with voltages lower than 1.3 V were not possible. On the other hand, when scanning the TiO₂ rutile (110) surface with voltages higher than 1.3 V the majority of the adsorbed oxygen molecules were dissociated during the first scan.

4.3.4 Stability of Oxygen Adatoms

After adsorption of oxygen molecules on the TiO_2 rutile (110) surface, the result visible with STM is the formation of oxygen adatoms on the five-fold coordinated titanium rows. These oxygen adatoms were found to be quite stable.

The STM image shown in Figure 4.13 was recorded after annealing the sample to 400 K. Although reference [52] reports that above 360 K titanium interstitial atoms are sufficiently mobile to form together with adsorbed oxygen excess TiO_x , none of the latter is visible in Figure 4.13. Still many oxygen adatoms cover the surface, which may result from inaccuracies of temperature measurements. This results from different reasons. One is that the thermocouple is fixed in some millimeters distance to the sample, and also the thermal conductivity between the crystal and the sample plate has an influence. In addition to this, the number of titanium interstitial atoms in the near-surface region, which depends on the reduction grade of the sample, influences the stability of oxygen adatoms on the TiO_2 rutile (110) surface. These facts explain the difference in the measured and the temperature reported in [52].

In order to test the stability of the oxygen adatoms, a voltage pulse of several volts was applied to an oxygen dosed TiO_2 rutile (110) surface.

In reference [25] it is mentioned that even short voltage pulses can locally "heal" a clean TiO_2 rutile (110) surface at ambient temperature. Due to the voltage pulse the bridging oxygen vacancies disappear. However, this does not work at low temperature. It turned out that at 78 K it is necessary to scan at least a small area at high voltage for producing a perfect TiO_2 rutile (110) surface without any bridging oxygen vacancies. In Figure 4.14 the same area on the crystal was imaged before (see Figure 4.14(a)), and after scanning a



(b) Linear fit of the data shown in Figure 4.12(a) (c) Adatom creation rate derived from the data shown in Figure 4.12(b)

Figure 4.12: Adatom creation measured in series of time-lapse STM images with the voltage kept constant at 1.3 V and varying the tunneling current. To obtain an adatom creation rate, the number of created adatoms per STM frame (and area) was counted. The different colors of the curves mark different tunneling currents, as indicated in the legend. The black data points show the average of all numbers of adatoms at the beginning and in the end of the measurements, respectively.

 $0.16 \, nA, 78.0 \, K$



Figure 4.13: Stability of the O_{ad} on the TiO_2 rutile (110) surface: The sample was heated to 400 K and O_{ad} are still clearly present. Imaging parameters: $30 \times 30 \text{ nm}$, 2.4 V, 0.15 nA, 17 K



(b) Imaging parameters: $20 \times 20 \text{ nm}^2$; 1.7 V, 0.16 nA, 78.0 K

Figure 4.14: High voltage (5.0 V/0.16 nA) scan of a small area of an oxygen dosed TiO₂ rutile (110) surface. At high voltage scanned area: $0.5 \times 0.5 nm^2$ indicated by a red box, 78 K

small area in the center at 5 V sample bias (see Figure 4.14(b)). In Figure 4.14(b) the area, which had been scanned at high voltage is easily recognizable in the STM image. Due to

the fact that the area without any defects in the center of the image exposes a nice square shape, this effect must be highly local. Figure 4.14(b) reveals another detail: Not only the bridging oxygen vacancies disappeared, but also the oxygen adatoms disappeared from the five-fold coordinated titanium atoms in the area, where the surface was scanned at high voltage.

This result shows that high voltage scanning of an oxygen-exposed rutile surface can be used as "locally cleaning scanning". This produces a perfectly stoichiometric surface on the scanned area, which can be used for performing future experiments.

4.3.5 Further Experiments

This section lists additional experiments, which have been attempted. Although they were not successful in the purpose they were performed, they could provide experimental parameters for future experiments or be pursued in the future after applying some improvements of the experimental setup of the LT-STM chamber.

Desorption Experiments

In reference [35] it was reported that two oxygen molecules can adsorb on the TiO₂ rutile (110) surface at a bridging oxygen vacancy (see chapter 2 and e.g., Figure 4.8). According to reference [35], these can then form a stable complex (O_4^{2-}) , which is called "tetraoxygen" (see also Figure 2.4 in section 2.1.1).

Tetraoxygen is expected to be still present at ambient temperature, because according to reference [35] it desorbs at temperatures higher than 400 K.

We attempted to find evidence for the proclaimed tetraoxygen using STM, but at high oxygen coverages no stable tunneling conditions could be established, possibly because a large amount of oxygen was adsorbed at the STM tip and oxidized it. However, at low oxygen coverages no evidence for the formation of tetraoxygen could be found with STM, which is in good agreement with reference [35].

Thus, we tried some desorption measurements. The sample was kept in the preparation chamber on the cold manipulator and then transferred to the heating stage, which was kept at ambient temperature to desorb physisorbed molecular oxygen. During the whole experiment the residual gas was analyzed with a quadrupole mass spectrometer. The pressure with respect to time for molecular oxygen (mass 32 amu) was recorded.

The sample was exposed to molecular oxygen at 105 K, then heated to ambient temperature. Then a UV-diode from outside the chamber shined onto the TiO₂ rutile (110) surface to desorb oxygen. Many attempts to "fine-tune" all parameters of the LT-STM system were performed, but for different reasons this setup is not suitable for measurements like the above mentioned. First, the mass spectrometer has no direct line of sight to the sample, which strongly affects the count rate. Second, the mounted quadrupole mass spectrometer is not suitable for this, because the pressure range needed to be changed during the experiment and this took the instrument several seconds. In this timespan, it was "blind" and did not record any signal. However, this experiment could possibly reveal interesting information, if it were repeated on a different experimental setup.

Laser Irradiation

This experiment was performed to test whether it is possible to non-thermally desorb oxygen adatoms from the TiO_2 rutile (110) surface. In a first step, the clean TiO_2 rutile (110) surface was exposed to oxygen to create the oxygen adatoms on the surface, and in the second step, a laser pulse was directed onto the crystal, which should transfer enough energy to the crystal to desorb the oxygen adatoms.

The laser was adjusted to a wavelength of 355 nanometers and pulses with different powers should provide the energy to excite electrons from the valence band into the conduction band. In addition to this the pulse energies were chosen in a way that the local heating of the sample was far below the limit of thermal annealing, even during the laser irradiation. A more detailed description of the power calibration of the laser are given in the Appendix section 7.2.

In these experiments the adatom coverage in monolayers before and after the laser irradiation was determined in STM images.



Figure 4.15: Oxygen adatom coverage after laser irradiation using different pulse energies. The underlying raw data is listed in table A 9 in the Appendix section 7.2.

This preliminary experiment led to the following results: Oxygen adatoms could be desorbed from the surface by laser irradiation. Figure 4.15 shows that a laser power of 15 mJ per pulse desorbs approximately 50 % of the oxygen adatoms, while for higher pulse powers approximately 90 % of the adatoms were desorbed, almost not depending on the pulse energy. The problem related to this series of experiments was that the laser pulse could not

be focussed only onto the sample, but also hit the sample plate and parts of the manipulator and desorb atoms from the residual gas there, which could hit the TiO_2 rutile (110) surface. In addition to this, the same desorption is possible with the reflection of the pulse to the inner chamber walls. This impurity effect was proved with a clean sample, which was irradiated without prior oxygen adsorption. After applying the laser pulse, many different adsobates could be identified in STM images. Therefore the above mentioned results only represent a tendency and mark a starting point for future oxygen adatom desorption studies using a pulsed laser. In addition to this no "healing" of bridging oxygen vacancies via diffusing oxygen adatoms was observed, as the number of bridging oxygen vacancies remained constant upon laser irradiation regardless the applied pulse of energy.

4.3.6 Discussion

DFT-based studies of molecular oxygen adsorbed on a TiO₂ rutile (110) surface had predicted that an O_2^{2-} molecule preferentially sits at an oxygen vacancy [54]. Further they postulated that the O₂ lies flat with its axis perpendicular to the rows at the vacancy site (see Figure 2.5(a) in section 2.1.1). Reference [44] reports a direct comparison of simulated Tersoff-Hamann plots of a clean, stoichiometric surface on the one hand, and a TiO₂ rutile (110) surface with an O_2^{2-} molecule in a bridging oxygen position on the other hand (see Figure 2.5(b)). The plots are remarkably similar one to the other, and support the assumption that the faint, smeared out feature in the STM images shown in Figure 4.6 is a direct observation of an oxygen molecule adsorbed in a bridging oxygen vacancy.

The equilibrium of this metastable, and very sensitive state can easily be disturbed. It is possible that the molecule suddenly explodes [89], and the two resulting oxygen single atoms could land on the five-fold coordinated titanium atoms, which are located next to the vacancy, as depicted in Figure 4.8. Again, this is a metastable, and even more sensitive configuration, while the energetically favored state would be one oxygen atom filling the vacancy, and the other one forming an adatom - the final state. This process happens quite frequently directly driven by the STM tip. As an evidence of this interaction, many, only partially visible "bean-shaped" adatoms are apparent (e.g., at the bottom of Figures 4.5 and Figure 4.8(c)). Another explanation for the "bean-shaped" adatom pairs can be found in a recent reference [53], which appeared after of our article reporting these results [1] was published. They claim that the bean-shaped adatom pair in STM images appears because of the still-intact oxygen molecule, which is switching between two positions. While one oxygen atom of the molecule in both cases remains in the bridging oxygen vacancy, the second forms an adatom on one of the neighboring titanium rows. This article [53] motivated a closer inspection of the data. However, no evidence for the proposed switching behavior was found.

The images revealed a clear relation between those faint, smeared-out features and oxygen adatoms, which appeared during scanning. Due to the temperature of 17 K adatom hopping could be excluded, and the number of faint, smeared-out features decreases with the same rate as the number of (created) oxygen adatoms on the surface increases. This motivated the conclusion that the faint features were assigned to oxygen molecules adsorbed

in bridging oxygen vacancy sites, because the freshly formed oxygen adatoms always form on a five-fold coordinated titanium site next to the spot, where in the previous image the faint features were located.

The STM allows to distinguish easily between across the row located "bean-shaped" adatom pairs that were originally one oxygen molecule adsorbed in a bridging oxygen vacancy, and a "pair" of independently formed adatoms, that meet on opposing titanium rows by chance. The STM images in Figure 4.7 show that there are clear differences in shape and brightness. In Figure 4.7(b) the two adatoms are separated by a bridging oxygen vacancy, while in image 4.7(a) the space in between the adatoms is occupied by a bridging oxygen atom. This difference clearly affects the image contrast, and based on extensive theoretical work about the role of excess charge in the oxygen adsorption, it seems also conceivable that the adatoms in both cases do not have the same charge.

The experimental results in Figures 4.5, 4.6, 4.7, 4.8 and 4.9 provide evidence that molecular oxygen can indeed be observed with STM, but also shows clearly that this species is only metastable. However, the STM measurement itself is the driving force of the most dissociation events, which have been monitored. All images have been recorded close to the temperature of liquid Helium.

Additional STM images were recorded at 78 K, and show essentially the same features: oxygen molecules at bridging oxygen vacancies could be identified as well as single oxygen adatoms, which suddenly appear during scanning (see Figure 4.11). But at this temperature only very few oxygen-vacancy-oxygen configurations could be observed, because they are very unstable and at this temperature already destroyed by the STM tip within the first scan. This fact proves that at 78 K the STM tip is even more likely to dissociate adsorbed oxygen molecules than at 17 K, and in many experiments the dissociation occurred already during the first scan and could therefore only be monitored indirectly by horizontal streaks in the images.

But what causes the facile dissociation of an adsorbed oxygen molecule during STM scanning? There are various mechanisms for tip-induced dynamics discussed in [90]. If an antibonding orbital is accessible for tunneling electrons, the dissociation rate should change linearly with the tunneling current. Taking into account local heating, the rate should scale like a power law I^n with a higher number of n.

The results presented in section 4.3.3 are a strong argument against the assumption that the dissociation is an electron induced process.

Nevertheless, a weak dependence on the tunneling current was observed. But this is an artifact of the measurement. A possible explanaition is the following: In a very basic assumption, the relation between the number of created adatoms to the number of scans is approximated by a function, which is steeper for a lower number of scans, and is converging asymptotically to the number of adatoms, where every adsorbed molecule on the surface is destroyed. If the tunneling current is low, the STM tip is further away from the sample, hence the electric field is lower and the influence to the sample is lower. Therefore the measurement is starting at a point of the above mentioned function, where it is steeper and the adatom creation rate seems higher. In contrast to this, at higher tunneling currents the influence of the STM to the surface is stronger and therefore it is plausible that already

before the first image a certain number of oxygen molecules are dissociated. This results in a starting point of the experiment closer to the asymptotic part of the assumed function and therefore the adatom creation rate seems to be lower.

This fact supports the assumption that the driving force for the interaction of the tip with the adsorbed oxygen molecule must be the electrical field between tip and sample. This parameter is related to the distance between tip and sample, and, hence, the logarithm of the tunneling current. Unfortunately there is no way to control the tip's shape and composition (e.g., an atom or a molecule could be adsorbed there). Thus, the local electrical field under the tip is different in every new approach, even when the tunneling parameters are kept constant. This explains why the large scatter of adatom creation rates was observed. As a consequence, the electrical field is likely the decisive factor in dissociation of an adsorbed molecule. One possible explanation would be that the molecule is pushed by the STM tip into a configuration, in which easy dissociation is possible. At this point it is still unclear what this configuration might be, but maybe if the molecule is shifted to a position closer to one of the substrate's titanium atoms, this could induce the dissociation. It is necessary to mention that for the setup in the LT-STM the product of any tip induced process could only be imaged if it is at least metastable on the surface on a timescale accessible to the STM. Thus, the tip helps to overcome the activation energy barrier, and gives a reason to believe that this process can also happen spontaneously at higher temperature. In this case the observed "bean-shaped" adatom pairs should be interpreted as an intermediate product of the dissociation of oxygen molecules on the TiO_2 rutile (110) surface, even in the absence of the STM tip.

In reference [36] desorption measurements are reported. They observed that the dissociation probability for oxygen molecules is related to their coverage, and that small amounts of O_2 on the TiO₂ rutile (110) surface dissociate more easily than large ones. For this reason, the oxygen dose was varied in the experiments as well, but there was no significant change in the adatom creation process or any new feature on the surface discovered. In a recent PSD/TPD study [36] it was reported that irradiation with above-band-gap photons not only desorbs molecular oxygen (via a hole capture process), but can dissociate them via an electron mediated process, too. In the same publication the creation of a "photoblind", thermally stable molecular oxygen species, which was attributed to "tetraoxygen" was hypothesized to be created upon photon exposure. With STM this species could not be found, neither by dosing higher amounts of oxygen, nor by irradiation of the surface with a UV-light emitting diode (365 nm, approximately 10¹⁵ photons cm⁻² s⁻¹).

Chapter 5 The Anatase (101) surface

We now turn to the from the catalysis point of view more interesting anatase polymorph of TiO₂. In this following chapter the TiO₂ anatase (101) surface is analyzed with STM. First the oxygen vacancies on the TiO₂ anatase (101) surface and in the subsurface region are studied. From theoretical studies it is already known that on the TiO₂ anatase (101) surface oxygen vacancies are less stable than in the bulk, which is clearly different to the rutile polymorph (see references [70, 19, 71]). Detailed experimental data about this phenomenon have not been available so far and therefore an STM study on this topic is presented in this thesis. When performing the experiments at 78 K, the oxygen vacancies can be stabilized on the surface and by gentle heating also their diffusion behavior can be monitored by recording series of time-lapse STM images.

Another interesting topic is the behavior of the TiO_2 anatase (101) surface when it is exposed to different gases. On rutile many of the adsorption and dissociation processes are known, but for the anatase polymorph the knowledge is rather sparse. The second part of this chapter reports detailed STM studies of the oxygen adsorption and the dissociation behavior on the TiO_2 anatase (101) surface. In addition to this, the adsorption of CO on the TiO_2 anatase (101) surface is analyzed.

5.1 Crystal Preparation

The TiO₂ anatase (101) crystal used in this work is a natural mineral sample. It was cleaved in ambient conditions (ex-situ) and exhibits a nice, flat (101) facet [91]. Due to a size of only $1.74 \times 0.96 \text{ mm}^2$ mounting the crystal on the sample plate was challenging, and also some experimental techniques were hard to use. Figure 5.1 shows the crystal in two different ways. Figure 5.1(a) shows the crystal mounted on a standard Omicron sample holder made from tantalum, while Figure 5.1(b) shows a photograph of the TiO₂ anatase (101) surface recorded via an optical microscope. It does not look like a perfect single crystalline surface, but if the areas with many steps and holes were avoided, it was possible to find large flat terraces, which were suitable for STM analysis.

In the first experiments the crystal was hardly reduced, and a flat, clean TiO_2 anatase (101)





(a) The anatase crystal mounted on an Omicron sample holder

(b) The anatase crystal

Figure 5.1: Pictures of the anatase crystal investigated in this work

surface was easily prepared by sputtering and annealing cycles similar to the preparation procedure described for the TiO_2 rutile (110) sample described in section 2.1. Sputtering was usually done with 1 keV Ar⁺ ions with a fluence of 6.7×10^{15} Ar⁺ ions per cm², and after sputtering the sample was annealed in UHV at 900 K using an electron beam heating stage. But after a large number of experiments it was almost impossible to achieve large terraces, and the number of defects also increased, because the crystal became gradually more and more reduced with increasing number of preparation cycles. Varying the sputtering parameters and annealing temperatures did not lead to an improvement. Finally a reoxidation using the following parameters was performed. The sample was heated to 930 K and exposed to molecular oxygen at quite high pressure $(5 \times 10^{-7} \text{ mbar})$ for 30 minutes. The parameters were chosen according to reference [92], where the reoxidation of a TiO_2 rutile (110) surface was successfully done. The same procedure led to also good results for the rutile crystal used in this work (see also section 2.1). First the reoxidation seemed to be the final solution to all problems with the crystal preparation. STM images recorded after this procedure showed large and almost defect-free terraces. So the sputtered crystal was reoxidized in every UHV annealing cycle. But after several preparation cycles, the quality of the resulting surface decreased again. In the images very often a rough structure was visible, which seemed to cover almost the whole surface (see Figure 5.2).

To get rid of this superstructure, several UHV annealing cycles at 970 K were performed. With increasing number of annealing cycles the superstructure vanished and revealed more and more of the clean TiO_2 anatase (101) surface. The temperature was chosen as a compromise between providing high enough mobility of the surface atoms to order, and reducing the sample at too high temperature. Figure 5.3 presents four different states of the crystal during preparation. Figure 5.3(a) was recorded right after sputtering the crystal



(a) Imaging parameters: $40 \times 40 \text{ nm}^2$, 1.5 V, 0.10 nA, 295 K



 (b) Line profile along the black line shown in 5.2(a). The indicated step height is resembling to the step height of TiO₂ anatase (101) crystals.

Figure 5.2: STM image of the observed rough structure on the TiO_2 anatase (101) surface after reoxidation

for ten minutes with 1 keV Ar⁺ ions and subsequent annealing at 920 K for 30 minutes. The surface looks fairly rough and contains a large number of small terraces. The following STM image in Figure 5.3(b) was recorded after reoxidation of the crystal at 920 K for 10 minutes at an oxygen pressure of 5×10^{-7} mbar. In contrast to the previous image (5.3(a)) the terraces are much larger and their shape is changing to triangular, which is typical for the TiO₂ anatase (101) surface (see reference [66]). A second ten-minute reoxidation cycle was performed, and the STM image in Figure 5.3(c) was recorded afterwards. The terraces are now bigger, and the number of step edges was reduced. Figure 5.3(d) presents the last image of this series, where the sample was reoxidized again (applying the same set of parameters used in the prior reoxidation). The terraces became a little larger, but the difference between Figures 5.3(c) and 5.3(d) is not very pronounced.

Finally, we found a reproducible procedure to prepare the surface, which granted a flat surface with large terraces. This was then be taken as a starting point for different series of experiments. The procedure is listed below:

- 1. Ar^+ sputtering with 1 keV for 10 minutes
- 2. reoxidising at 920 K for 20 minutes
- 3. switching off the O_2 and wait until the pressure in the chamber recovers below 5 $\times 10^{-9}$ mbar before switching off the heating



(a) STM image recorded after sputtering and annealing at 920 K for 30 minutes. Imaging parameters: $500 \times 500 \text{ nm}^2$, 2 V, 0.15 nA, 79 K



(b) STM image recorded after reoxidation ($p_{O_2} = 5 \times 10^{-7}$ mbar, 920 K, 10 minutes). Imaging parameters: 500×500 nm², 2 V, 0.15 nA, 79 K



(c) STM image recorded after additional 10 minutes reoxidation using the same parameters as in Figure 5.3(b). Imaging parameters: $500 \times 500 \text{ nm}^2$, 2V, 0.15 nA, 81 K



(d) STM image recorded after additional reoxidation using the same parameters as in Figures 5.3(b) and 5.3(c). Imaging parameters: $500 \times 500 \text{ nm}^2$, 2V, 0.15 nA, 82 K

Figure 5.3: STM images of of the TiO_2 anatase (101) surface recorded after different preparation steps (see text)

4. several annealing cycles (10 minutes) at 900 K

For the experiments mentioned in this work, the full preparation procedure was not performed before every single experiment. In our experiments were no gases adsorbed, which would form a stable adsorbate and could only be removed by ion sputtering. So the full procedure was performed once a week. For several days afterwards the same surface could be re-established by ten minutes UHV annealing at 900 K.

5.2 Characterization of the Anatase Sample

The state of bulk reduction of the anatase sample was determined via x-ray photo-electron spectroscopy (see section 3.1.5). In Figure 5.4 three different XPS spectra are presented. They are all normalized to enable a direct comparison in the graphs. The anatase spectra were recorded to determine the surface composition and to obtain more information about the reduction state of the sample (oxygen deficiency and excess titanium atoms). When the crystal is reduced, two major defects are occurring in the near surface region: oxygen vacancies and excess titanium atoms, which are occupying interstitial positions in the near surface region. Thus, the XPS spectra were recorded to gain information about the number of oxygen vacancies and titanium interstitial atoms. This information is needed because DFT calculations predict different adsorption properties for oxygen in the vicinity of a titanium interstitial atom (see reference [76]). The color code indicates the different preparations of the samples: The red curve shows the intensity of the Ti2p peak of a sputtered and annealed TiO_2 anatase (101) surface. The blue spectrum represents the freshly reoxidised TiO_2 anatase (101) surface, while the black curve shows the signal recorded from a TiO₂ rutile (110) reference sample. Compared to the spectrum of the TiO₂ rutile (110) surface, in both anatase spectra a clear shoulder is visible at the low binding energy side of the Ti2p peak. This is an indication of surface reduction (Ti^{3+}) and can stem either from interstitial titanium atoms or oxygen vacancies in the near-surface region. Due to the size of the sample only normal incidence XPS was possible, and a quantitative determination of the Ti³⁺ signal could not be performed.

After preparation, the sample was investigated with LEED (see section 3.1.3) to determine the quality of the surface. The LEED image in Figure 5.5 shows a clear, sharp pattern of the TiO₂ anatase (101) surface at 100 eV electron energy, which is in good agreement with a LEED pattern presented in reference [93].

To further verify the cleanness of the sample, also an AES spectrum (see section 3.1.2) of the TiO_2 anatase (101) surface was recorded. The primary energy of the electrons was 3 keV and the differentiated intensity *versus* AES electron energy plotted in Figure 5.6 shows a typical spectrum.

The spectrum in Figure 5.6 shows peaks for titanium and oxygen as expected [86]. The spectrum was also analyzed for peaks of commonly known impurities of TiO_2 as potassium, calcium, aluminum and magnesium. But even the strongest Auger peaks of these impurities were absent in the spectra, which indicated that the surface was clean. In the AES spectra



Figure 5.4: XPS spectra of different preparations of the TiO₂ anatase (101) surface compared to the spectrum of a TiO₂ rutile (110) sample. Blue line: anatase annealed in UHV for 10 minutes at 970 K; Red line: anatase reoxidised at an oxygen pressure of 5×10^{-7} mbar at 945 K



Figure 5.5: Photograph of the LEED pattern of the clean, as prepared TiO_2 anatase (101) surface

of a different TiO_2 anatase (101) sample a large peak of iron was identified, but the spectra for the sample used for the experiments presented in this thesis did not show any iron contamination. Despite this result, black spots were identified on the TiO_2 anatase (101)



Figure 5.6: differentiated AES spectrum of a clean sputtered and annealed TiO_2 anatase (101) sample

surface (see Figure 5.7), which were later identified as possibly iron impurities. In this case the amount of iron was below the detection threshold of the AES setup installed in the LT-STM system.

STM images of the clean, freshly prepared TiO₂ anatase (101) surface often exhibit two major forms of defects: Bright spots, which span over several surface unit cells, and (almost) triangularly-shaped dark spots (see red box and small insets in Figure 5.7). On freshly prepared TiO₂ anatase (101) surfaces the bright defects are not always present and their density is much lower than that of the dark spots. In a first assumption the dark spots in STM images of the TiO₂ anatase (101) surface like Figure 5.7 were assigned to defects in the subsurface region, because according to [71], the stability of defects on the TiO₂ anatase (101) surface is energetically less favorable than in the bulk (see also references [19, 70]). In STM images the surroundings of the black spots is much brighter than the undisturbed surface. This might be explained by a space charge caused by a defect or a dopant in the surface region of a semiconductor. A space charge is a local inhomogeneity of charge carriers, which changes the position of the energy bands. Therefore different states of the sample are taking part in the tunneling process and the STM tip reads a different contrast. This effect is called "band-bending" and a detailed review about its properties is found in reference [94].

However, XPS data in follow-up experiments on a different TiO_2 anatase (101) sample indicated that the black spots were impurities on the surface and no subsurface defects. XPS data suggest that the impurity could be iron, which segregates from the bulk during annealing at temperatures higher than 400 K, but this still needs to be confirmed. In contrast to the bright defects, the dark ones can be found in (almost) every preparation, and are spread very unevenly over the whole surface (see Figure 5.7).



Figure 5.7: STM image of the clean, as prepared TiO_2 anatase (101) surface. The red box indicates one of the dark defects, which are unevenly spread over the surface. The small insets below show magnifications of one of the dark defects recorded with different scanning voltages. Imaging parameters: 44×44 nm², 1.5 V, 0.13 nA, 79 K

In the STM images in the lower part of Figure 5.7, the same spot is scanned several times at different tunneling voltages. The current was fixed at 0.5 nA, while the voltage was varied between 0.6 and 1.4 V. It shows that the black defects are imaged very differently by different tunneling conditions. While they are easy to identify for tunneling voltages above 1 V, they can almost vanish for lower values. Further, in series of STM images, which were recorded at various temperatures (between 77 and 295 K), over a time span of several tens of minutes, no diffusion of those black defects could be observed.

5.2.1 CO Adsorption

In order to perform the oxygen adsorption studies on the TiO_2 anatase (101) surface, it was necessary to gather knowledge about the most common impurities in the residual gas of the UHV setup. The adsorption of water was already discussed in section 2.2.1. Therefore a series of CO adsorption experiments was done. The goal of these experiments was to find out the adsorption position and the appearance in STM of CO in order not to misinterpret later recorded images where the oxygen adsorption was studied. The CO was dosed via a leak valve directly into the analysis chamber and adsorbed on a freshly prepared TiO_2 anatase (101) surface at 105 K. STM images indicated that already a nominal dose of 0.18 L of CO forms a full monolayer on the TiO_2 anatase (101) surface.



Figure 5.8: STM image of the TiO₂ anatase (101) surface with a full coverage of CO; Imaging parameters: $40 \times 40 \text{ nm}^2$, 1.3 V, 0.15 nA, 78 K

In order to gain information about the site where the CO molecules adsorb on the surface, the dose was drastically lowered. A dose of 0.002 L of CO a resulted in a surface coverage where the substrate was still clearly visible and enough CO molecules were adsorbed to gain more information about the adsorption site. A typical STM image is shown in Figure 5.9.

Recording STM images with CO on the TiO_2 anatase (101) surface turned out to be rather hard, because already really sensitive tunneling parameters caused the CO molecules to diffuse on the TiO_2 anatase (101) surface. On the one hand this can be caused by "pushing" the adsorbed molecules with the tip. On the other hand it is conceivable that the tip electrostatically attracts an adsorbed CO molecule, which weakens the binding to the surface, and induces the diffusion in this way. However, a sample bias voltage of 1.3 V and a current lower than 0.06 nA were found to be gentle enough to produce nice images without tip-



Figure 5.9: CO on the clean TiO_2 anatase (101) surface; Imaging parameters: $40 \times 13 nm^2$, 1.3 V, 0.085 nA, 78 K

induced diffusion of the CO molecules. Using these parameters, the STM image shown in Figure 5.10 was recorded. The grid represents the lattice to clarify the adsorption position of the CO molecule on the TiO₂ anatase (101) surface. In the STM images two different modifications of the adsorbed CO molecules could be identified, which are indicated by the red and the blue box in Figure 5.10. But these STM images were misleading. The difference in the shape of the CO molecules can be explained by band bending, which is changing the contrast and therefore different shapes and heights in the STM images can be observed.



Figure 5.10: STM image to indicate the adsorption position of CO molecules on the TiO_2 anatase (101) surface. The red box indicates a "half-moon" shaped CO molecule, while the blue box shows a "heart-shaped" one. $7 \times 5 nm^2$, 1.3 V, 0.085 nA, 78 K

After obtaining information about the adsorption site on the TiO_2 anatase (101) surface also the thermal stability of CO molecules on the surface was analyzed. In Figure 5.11 the coverage of the surface with CO is plotted versus temperature.

To gain information about this process, first an STM image was recorded and the number of CO molecules in monolayers was determined. Then the sample was heated to the specified temperature for ten minutes and another STM image was recorded. Again the coverage in monolayers was determined and the fraction of these two values gives the value shown in Figure 5.11. From this data a rough estimation of the activation energy was calculated as $0.31 \,\mathrm{eV}$.

Discussion

Apparently the sticking coefficient of CO on the TiO_2 anatase (101) surface is much higher than the one for molecular oxygen using the same dosing parameters (see chapter 5.3.2).



Figure 5.11: Temperature dependence of the CO desorption from the TiO_2 anatase (101) surface. The underlying raw data is shown in the Appendix section 7.1.

However, in the STM images, it seemed that there are two possible adsorption configurations possible for adsorbed CO molecules. In Figure 5.10 the two different shapes are indicated by a red and a blue box, respectively. A careful analysis of the STM images revealed that the two different adsorption configurations are only one, but due to the band bending on the TiO₂ anatase (101) surface due to subsurface defects or impurities the adsorbed CO molecules appear different in the images. This hypothesis is also supported by the fact that the CO molecules in both configurations adsorb at the same position on the TiO₂ anatase (101) surface (see 5.10). The preferred adsorption spot is the five-fold coordinated titanium atom on the "mini terrace" of the sawtooth.

Another important result is that CO already desorbs from the surface well below 150 K. This result is very important in the field of the oxygen adsorption (section 5.3.2). An inevitable source of CO in an UHV chamber are the chamber walls and the ion pumps. In general this is not a serious problem, but when dosing oxygen, an exchange reaction can take place there and oxygen molecules can substitute CO molecules on the inner chamber walls or the ion pump surface. The substituted CO molecules can then adsorb onto the sample. This mechanism is important to take into account when adsorbing oxygen on a surface, because of the large difference of the adsorption coefficients of the two gases on the TiO₂ anatase (101) surface.

5.3 Results and Discussion

5.3.1 Electron Induced Surface Oxygen Vacancies

Producing Surface Oxygen Vacancies by Electron Bombardment

In section 2.2 it was already mentioned that surface oxygen vacancies on the TiO_2 anatase (101) surface are thermodynamically not favored. At ambient temperature it was shown in reference [72] for the TiO_2 rutile (011) surface that surface oxygen vacancies can be created not only via sputtering, but also via a Desorption Induced by Electronic Transition (DIET) process. This process was described by M. Knotek and P. Feibelman on TiO_2 crystals (see reference [95]). The Knotek-Feibelman process demands a repulsive excited state, which also lives long enough to enable nuclear motion on the surface. Further the probability for the occurrence of it is higher for the most undercoordinated and most exposed surface atoms, where the excitation lives longest. Therefore the two-fold coordinated oxygen atoms are prominent candidates for being desorbed. The model proposed in reference [95] is based on the observation that the excitation energy of a core hole and the threshold energy for Electron Stimulated Desorption (ESD) of O^+ ions from TiO_2 are quite similar. The formation of the O⁺ ion from the formally two-fold negatively charged surface oxygen atom is explained there by an inter-atomic Auger process, in which electrons from the O2porbitals from a different oxygen atom fill the titanium core orbital. The usually much faster intra-atomic process, where electrons from a higher titanium level decay into the core hole is impossible for an empty Ti3p hole. In the rare case that three electrons leave the surface oxygen atom, e.g., via a double Auger decay, the atom becomes an O^+ ion and is repelled by the surrounding Ti^{4+} lattice atoms and ejected from the crystal (see also reference [72]). This process is also generalized to other surfaces like V_2O_5 , WO_3 , Cr_3O_3 or NiO [95].

Nevertheless, the surface oxygen vacancies can be, similar to the rutile, the active centers on the surface. They are created by a DIET process, but are quite reactive and interact with water vapor and possibly also with other gases from the residual gas in the UHV chamber. In order to avoid any influence by adsorbates the requirements to the vacuum during irradiation are really challenging. It is absolutely necessary to degas the electron gun thoroughly for several hours to minimize the probability of adsorbing any unwanted species during the bombardment onto the freshly activated surface. In order to hinder the created surface oxygen vacancies from migrating into the bulk, the crystal was kept at 105 K during irradiation.

The electron bombardment was done by using a rasterable electron gun with a current density of $8 \,\mu\text{A} / \text{cm}^2$. An electron energy of 500 eV was found to be ideal for creating surface oxygen vacancies. It was a compromise between reducing the energy as much as possible to be able to create a low, but easily reproducible density of surface oxygen vacancies, and keeping the energy high enough to get a reasonable sample current image which was used to ensure that the electron beam hits the sample. The same sample current image is used to adjust the ion beam for sputtering; see also section 2.1. In order to measure the correct sample current, a positive sample bias of 27 V with respect to ground had been

applied to it during the electron irradiation. Thus the calculated electron flux was 6.92 $\times 10^{13}$ electrons per square centimeter and second. Thus the overall dose for 300 seconds irradiation resulted in 2.08 $\times 10^{16}$ electrons per cm². After the bombardment, the sample was transfered to the STM for surface analysis as fast as possible, but nevertheless the first STM image could only be recorded about ten minutes after the end of the irradiation. In the images a uniform distribution of bright defects could be observed. The determination of the density of defects on the surface (approximately 8% of a monolayer), together with the electron flux calculated before, led to a total estimated cross section for the defect yield by electron bombardment of 4.02×10^{-18} cm². The cross section expresses the probability for an incoming electron induce a DIET process and to desorb a two-fold coordinated oxygen atom from the TiO₂ anatase (101) surface. Figure 5.12 shows a typical STM image recorded after the irradiation.



Figure 5.12: Electron irradiated TiO_2 anatase (101) surface at 78 K. The white features are the surface oxygen vacancies, which have been created by electron bombardment at 105 K. Imaging parameters: $26 \times 26 \text{ nm}^2$, 1.5 V, 0.25 nA, 78 K

The surface oxygen vacancies produced by electron bombardment span two lattice sites along the [010] and two in $[10\overline{1}]$ direction. In agreement with DFT-based calculations [19, 70] and simulated Tersoff-Hamann STM images performed by U. Aschauer and A. Selloni these features were assigned to vacancies of two-fold coordinated oxygen atoms on the edge of the sawtooth (see Figures 5.13 and 5.12, and also section 2.2). The DFT calculations were performed by using the Quantum ESPRESSO package [96], the PBE0 functional [97] and a mixed localized and plane wave basis set expansion of the electronic states as implemented in CP2KQUICKSTEP [98].

Figure 5.13 shows excellent agreement between the simulated and the measured STM images.



(a) Simulated STM image of an oxygen vacancy (b) Magnified STM image of an oxygen vacancy on the TiO_2 anatase (101) surface (Simulation performed by U. Aschauer)



on the TiO_2 anatase (101) surface

Figure 5.13: Comparison of a simulated and a measured STM image of an oxygen vacancy on the TiO_2 anatase (101) surface

Thermal Stability of Surface Oxygen Vacancies

On the electron irradiated surface described in section 5.3.1, two different experiments have been performed.

The first was done to determine the stability of surface oxygen vacancies on the TiO_2 anatase (101) surface with respect to temperature and to estimate the activation energy barrier for subsurface migration. After determination of the initial defect concentration after electron irradiation, the sample was heated on the manipulator to a specified temperature for ten minutes. To achieve a stable thermal equilibrium, the manipulator was thermally equilibrated to the desired temperature either by cooling with liquid nitrogen or resistive heating, or sometimes even both, before inserting the sample. In addition to this the wobblestick used to transfer the crystal from the STM to the manipulator and back was cooled, in order not to introduce a source of systematic error in the measurement. Continuing the experiment, the sample was then put back to the STM and after cooling to 78 K, the number of remaining defects was counted. The ratio of those two defect densities was then determined and is plotted in Figure 5.14.

From Figure 5.14 it can be deduced that the migration of defects to the subsurface region starts at approximately 200 K, and at temperatures above 500 K, all defects have already vanished from the TiO_2 anatase (101) surface.

In the second series of experiments, the stability of the defects over time was investigated. Therefore the oxygen vacancy concentration was determined in series of STM images recorded at different temperatures. In addition to this the concentration of those features with respect to time after irradiation was monitored. From determining the density of oxygen vacancies in series of consecutive, time-lapse STM images, it was concluded that the total density of defects is constant within statistical variation for a timespan up to 3000 seconds (see Figure 5.15).

This is an important result, because it gives evidence that at in the investigated temperature range the density of oxygen vacancies is constant for the timescale of the performed experiments. Therefore no further decay laws to model the decay of surface defects over time must be taken into account.

When the electron bombarded sample was heated to temperatures higher than 320 K most of the surface oxygen vacancies disappeared. However, in the temperature range between 320 and 500 K a new feature appeared (see Figure 5.16). This feature could always be observed in this temperature interval, but the pronunciation of the "tentacles" was sometimes different. Perhaps in the subsurface region charged defects accumulate depending on the sample's preparation history and also on the annealing temperature, which therefore cause the apparent shape of these features. The numbers of these features were not counted as defects for Figures 5.14 and 5.15.

In addition to this, another interesting phenomenon was found: It could be observed that an oxygen vacancy vanishes from the surface and reappears after some time at the same position. This is illustrated in Figure 5.17.

The series of time-lapse STM images shows seven surface oxygen vacancies on the TiO_2 anatase (101) surface over a time span of 77 minutes. Six of them stay at the spot where they were observed in the first image. But one of them (indicated by a red arrow) suddenly disappears and leaves back a defect-free TiO_2 anatase (101) surface (yellow arrow). After some minutes at the same position where the vacancy vanished, a vacancy appears.



Figure 5.14: Decay curve of the electron-induced defects as a function of temperature. The underlying raw data is shown in Table A 6 in the Appendix (section 7.1).
The following series of experiments was done on the same crystal, which was prepared in the same way as for the first experiments. But in this case, the whole STM was heated to temperatures between 223 and 301 K. Again series of consecutive STM images were recorded, and the number of defects was counted in each single image. It was observed that at higher temperatures the total defect concentration was lower than at 78 K, and also diffusion of oxygen vacancies on the TiO₂ anatase (101) surface was monitored. However, a stable, but dynamic equilibrium of defect concentration could be found for every investigated temperature, where the numbers of vanishing and appearing defects are equal (see Figure 5.15). Further the "hopping rate" of oxygen vacancies with respect to temperature was analyzed.

Figure 5.18 shows the number of migration events (appearance and disappearance) per defect and frame observed in series of time-lapse STM images related to the total number of defects visible in the images. The recording time per frame was approximately 80 seconds. The graph clearly shows that the onset of the defect diffusion is at ≈ 200 K. Due to the fact that the coverage of surface oxygen vacancies was low, and only one vacancy concentration was studied, the influence of the defect concentration on the migration behavior could not be investigated.

Despite the fact that the sample preparation was always done in the same way, the STM



Figure 5.15: Stability of electron induced defects over time. The raw data are shown in Table A 2 in the Appendix section 7.1.



Figure 5.16: STM image of a sample with O_{vac} 's after heating an electron irradiated TiO_2 anatase (101) surface higher than 320 K. Image parameters: $17 \times 17 \text{ nm}^2$, 0.8 V, 0.14 nA, 78 K



Figure 5.17: Consecutive STM images monitoring seven O_{vac} 's on the TiO₂ anatase (101) surface (77 minutes total recording time). The red arrows point to one of them, which diffuses subsurface (indicated by the yellow arrow) and reappears later. Image parameters: $4 \times 4 \text{ nm}^2$, 1.6 V, 0.21 nA, 259 K

images, where the whole STM setup was heated, show lower coverage of surface defects. At lower temperature the coverage was higher, while for higher temperatures it decreased. This supports the theory that the number of defects is not constant, but some dynamic, temperature dependent equilibrium. In series of STM images recorded at higher temperatures, it was observed that they are quite mobile and diffusing from and to the surface. In the temperature range from 200 to 300 K the hopping probability increases almost exponentially (see Figure 5.18). It also seemed that they could diffuse on the surface, and therefore a mathematical model to calculate the activation energy barrier for surface diffusion was tested. In reference [99] a model for surface diffusion was proposed, performing a one dimensional random walk, of catechol on a TiO₂ rutile (110) surface. The model was adapted and tested for the diffusion of oxygen vacancies on the TiO₂ anatase (101) surface, but unfortunately the result was inconclusive. The most probable explanation for this is that in reference [99] there was a molecule performing a one dimensional random walk only on the surface, which is thought as a rigid and impermeable plane for the molecules. In contrast, the oxygen vacancies in the experiment described in this work preferably diffuse



Figure 5.18: Hopping events per defect and frame depending on the sample temperature

to the subsurface region and pop up again. During the time the vacancy is below the surface, it is invisible for STM, which points out the problem of this method: It is impossible to distinguish between a single vacancy migrating subsurface and back up again at some close-by place and two independent vacancies, of which one diffuses subsurface and the other in reverse direction to the surface in close vicinity. Another problem with this kind of experiment is the limited resolution of the time-lapse STM images with respect to imaging time: *e.g.*, if there is a vacancy imaged in one image, it could vanish and reappear until the tip scans it again, and in the two images there is no visible difference, which is interpreted as no diffusion event.

Discussion

The first crucial point for all experiments was the time between electron irradiation and the first STM image. In the LT-STM setup it took at least ten minutes to record the first STM image after electron irradiation. Within this time span the oxygen vacancy density decreases significantly, as shown in Figure 5.14. This also explains the different vacancy densities found in independent experimental runs for Figure 5.15.

Another important result is shown in Figure 5.15. Despite the rapid decrease of the vacancies in the first ten minutes, the total number of oxygen vacancies on the TiO_2 anatase (101) surface remains constant throughout one entire experiment. Thus, no exponential law to determine the further decay of the surface oxygen vacancy density throughout one single experiment was necessary. This also supports the assumption that the determined densities of surface oxygen vacancies in Figure 5.14 indeed show the equilibrium concentration at the given temperatures. These facts and the mechanism presented in Figure 5.17 led to the conclusion that there is a dynamic equilibrium of surface vacancies.



Figure 5.19: Models for the temperature stability of the O_{vac} 's created by electron beam bombardment. The dashed line in the graph shows the expected behavior with an assumed activation energy barrier for the subsurface migration of 0.75 eV. The solid, blue line shows the fit of the experimental data (presented in Figure 5.14) using the rounded trapezoidal shaped distribution of activation energies derived in the Appendix section 7.2.

Figure 5.19 shows the experimentally found temperature dependent decrease of the surface oxygen vacancies. DFT predicts a much steeper decay than the experimental result shows. The dashed line in Figure 5.19 shows the decay curve of surface oxygen vacancies on the TiO₂ anatase (101) surface for a single activation energy barrier of $0.75 \,\text{eV}$, as predicted by DFT [70]. The discrepancy between the predicted curve and the experimentally found results is explained by the following: First, theory assumes a perfect TiO₂ anatase (101) slab for the calculations and does not take care of other defects than the surface oxygen vacancy under investigation. Further there is no reason for the vacancy to remain on the surface, once the temperature is high enough to overcome the activation energy barrier for subsurface migration. And there is little reason for the vacancy to migrate back to the energetically less favorable position on the surface. In contrast to this, in the experiment disappearing and reappearing surface oxygen vacancies have been observed (see Figure 5.17). These exhibit a dynamic equilibrium, which is hard to model in DFT calculations. In addition, in the experiment there are always subsurface defects and interstitial titanium atoms present, which influence the activation energy barrier locally.

The uneven appearance of the STM images of the clean TiO_2 anatase (101) surface (see Figure 5.7) is explained by local band-bending effects. Therefore at least a certain number of subsurface defects is charged, which can pose a considerable influence to the energetics

and dynamics of the defects migration behavior in the vicinity. Thus it is justified to assume a range of activation energy barriers for the migration to the subsurface region of the surface oxygen defects. The solid, blue line in Figure 5.19 shows the calculated temperature dependence of the surface vacancy concentration, assuming a rounded trapezoidal distribution of activation energies in the range from 0.6 to 1.2 eV, as shown in the inset in Figure 5.19 (see also mathematical model in the Appendix section 7.2).

Oxygen adsorption experiments (see section 5.3.2) resulted in the estimate that the density of interstitial titanium atoms and surface vacancies in the near-surface region of the sample amounts to $2 \pm 1 \%$ of a monolayer on the clean TiO₂ anatase (101) surface.

Also the behavior of the surface oxygen vacancies with respect to time and temperature are well explained by a range of activation energy barriers. For an initial vacancy concentration, where a defect is located at a locally perfect region on the surface, a vacancy can migrate subsurface at temperatures higher than 200 K, which alters the activation energy for subsurface migration for a different defect in the vicinity. Further it is considered plausible that an oxygen vacancy can diffuse within the subsurface region of the sample for a certain distance (with newer results for the activation energy barrier interval (1.1 to 1.8 eV) [100], compared to the ones reported in reference [70] (0.74 and 0.95 eV), see also section [70]), before popping up on the surface again. This was also observed in the experiment.

When the irradiated surface was heated, new features were observed in the temperature range from 300 to 500 K. These new features possibly show an aggregation of oxygen vacancies in the near-surface region, which alters the LDOS and therefore can be imaged with STM. The parameters of subsurface diffusion of oxygen defects and the temperature dependent equilibria, which were experimentally observed, could also be affected by the initial vacancy concentration, but this question was not in the scope of this thesis and could be studied in future experiments.

5.3.2 Oxygen Adsorption

It was already mentioned in the context of the experiments performed on the rutile crystal, reported in chapter 4 that oxygen interacts only weakly with a perfectly stoichiometric oxide surface [46, 101]. To adsorb an oxygen molecule on the surface, excess electrons, which can be transfered to the adsorbed species, are necessary. These electrons can stem from intrinsic defects, as *i.e.*, oxygen vacancies or titanium interstitial atoms, or from hydroxyls or photo-excited electrons [51, 77]. Depending on the number of available electrons, molecular oxygen can therefore adsorb as O_2^- or as O_2^{2-} (see reference [76]). Conversely, negatively charged oxygen adatoms can facilitate the diffusion of interstitial titanium atoms to the surface. At elevated temperatures these titanium and oxygen atoms form excess TiO₂, which can also grow in non stoichiometric and disordered configurations (see Figure 5.2). Reference [102] reports DFT-based calculations (using the CASTEP code) indicating that oxygen adsorption on a pristine TiO₂ anatase (101) surface is taking place atop of the five-fold coordinated surface titanium atoms. The favorable adsorption configuration is with the oxygen molecule lying flat on the mini terrace of the sawtooth with the two oxygen atoms each bound to one five-fold titanium atom. In a private communication U. Aschauer stated that the O_2^{2-} can react with a subsurface oxygen vacancy and thus can form an oxygen dimer at the two-fold coordinated oxygen site on the surface. Reference [102] also states that oxygen adsorption is energetically more favorable on the (001) surface than on the TiO₂ anatase (101) one.

The oxygen exposure of the crystal was performed by dosing molecular oxygen to the freshly prepared sample on the cold manipulator in the preparation chamber. Typical dosing parameters were the following: 90 L of oxygen at 105 K. After the exposure the sample was immediately transfered into the STM and the tip approach was initiated.

In the first oxygen adsorption experiments an extremely high surface coverage with oxygen was observed in STM images (see Figure 5.20).



Figure 5.20: STM image of first oxygen adsorption experiment on the TiO₂ anatase (101) surface. It turned out later that most of the observed species were CO. Imaging parameters: $40 \times 40 \text{ nm}^2$, 1.8 V, 0.1 nA, 78 K

In order to test the reliability of these STM images, a LEIS spectrum of the adsorbed oxygen on the sample's surface was recorded with labeled oxygen. This experiment should provide the possibility to quantify the total amount of oxygen on the as-prepared TiO_2 anatase (101) surface.

This experiment was carried out in the PINUP system. The sample was prepared as usual, except the oxygen dosing was different. Instead of the regular oxygen gas the same dose, which was used in the other experiments, of isotopically labeled oxygen ($^{18}O_2$) was dosed. In LEIS measurements, the signal of each atomic mass is recorded separately. In this case the mass of the oxygen atoms on the surface would be 18 amu (Atomic Mass Unit) instead of 16 amu for normal atomic oxygen. The ratio of the two masses (18 and 16 amu for labeled and standard oxygen, respectively) should then provide information about the total surface coverage with adsorbed oxygen molecules.

For this experiment first the purity of the ${\rm ^{18}O_2}$ and the ratio compared to the normal ${\rm ^{16}O_2}$ was measured.

Figure 5.21 shows the spectrum recorded with the quadrupole mass spectrometer. Normally the isotope ¹⁸O₂ is very rare and in standard oxygen gas the content of this isotope is only 0.2% [103]. In the presented spectra it is obvious that the fraction of atomic ¹⁸O and the molecular ¹⁸O₂, respectively, compared to the standard oxygen with atomic mass ¹⁶O (and molecular mass ¹⁶O₂) is higher. The ratio of ¹⁸O₂ : ¹⁸O¹⁶O : ¹⁶O₂ is determined from 5.21 as 1 : 0.13 : 0.03. Thus follows that the percentage of ¹⁸O in the dosed gas



Figure 5.21: QMS spectrum to determine the purity of the ¹⁸O gas at a pressure of 2×10^{-8} mbar.

is 90.09 %. Therefore it should be possible to obtain a signal stemming from the labeled oxygen adsorbed on the TiO₂ anatase (101) surface.

Due to the tiny size of the sample, focusing the ion beam onto the TiO_2 anatase (101) surface was almost impossible. In addition to this the position of the sample changed when the manipulator was cooled. At 100 K the manipulator contracted in a way that the surface, which had been in the center of the ion beam at room temperature was completely out of focus.



Figure 5.22: LEIS spectrum of ${}^{18}O$ and ${}^{16}O$ adsorbed on the TiO₂ anatase (101) surface

The energies for ${}^{18}\text{O}$ and ${}^{16}\text{O}$ for 1 keV helium ions and an the angle of 120° between the ion

source and the analyzer in the PINUP system have been calculated according to equation (3.8) in section 3.1. The values are 507 and 463 eV, respectively. To test the formula, the energies were also calculated using the LEIS energy calculator provided at reference [104]. The curve shows a ratio of ¹⁸O to ¹⁶O of 12%, which is significantly higher than the usual ratio of 0.2%, but well below the high coverage shown in the STM image in Figure 5.20. Due to the above mentioned experimental problems, also ¹⁸O atoms adsorbed on the sample plate may have contributed to the value found. Therefore, surface coverage with oxygen is assumed to be well below 10 percent of a monolayer.

As a consequence further experiments have been performed to determine the reason for the high coverage and to find out what caused the high surface coverage observed in the STM image in Figure 5.20. CO adsorption experiments (described in section 5.2.1) showed that the latter adsorbate was the reason and therefore in all experiments listed below, the sample was flashed to 200 K after oxygen exposure to get rid of the co-adsorbed CO.

In STM images recorded after dosing oxygen, several new species could be distinguished, see Figure 5.23.

The big majority of new features are double spots with an apparent separation of less than two neighboring lattice positions, which are centered on the position of a two-fold coordinated surface oxygen atom (red box in Figure 5.23). Often these "dimers" are surrounded by a dark halo in STM images. The extent and depth of these halos depends on the tunneling conditions in a similar way as the black defects on the clean surface do (see section 5.2). Another feature consists of two or more single dimers (see green box in Figure 5.23). These features are usually surrounded by larger and darker depressions. The black box marks an impurity, which was already discussed in section 5.1. The purple box finally marks the third newly found species, which looks like a star on the surface. It is centered at the position of a five-fold coordinated titanium atom and spans over several lattice sites.

Figure 5.24 shows the magnification of the two dominating features visible on the TiO_2 anatase (101) surface after oxygen exposure at 105 K. Figures 5.24(a) and 5.24(b) also indicate the underlying crystal lattice to clarify the position of the double and the star-like features, respectively.

In order to probe the stability of these features with respect to temperature, the sample was heated on the manipulator to specified temperatures for ten minutes, following the procedure described in detail in section 5.3.1. It turned out that the total density of defects on the surface remains constant up to a temperature of 500 K (see Figure 5.26, below). But there is a significant change in the images: the fraction of dimers to star-like features is altered. In the images recorded right after oxygen exposure at 78 K, ratios of dimers to star-like features from 1:1 to 4:1 have been observed, with an average value of 2:1. Above a temperature of 325 K, however, a decrease of star-like species was observed, while a new species could be identified. Additional bright, circular shaped features appear on the surface. The percentage of the altered features and the extra bright ones increases with temperature at expense of the star-like species, while the number of dimer-like features was not affected by this process.

In Figure 5.25 the same color code as in Figure 5.23 is used. In addition to this, the



Figure 5.23: Oxygen dosed TiO_2 anatase (101) surface. The different new species are indicated by colored boxes. Blue box: Star-like feature of an oxygen dimer at the spot of a five-fold coordinated titanium atom; green box: Two neighboring adsorbed oxygen dimers with stronger band-bending than single ones; red box: O_2 molecule adsorbed at an impurity on the surface; black box: impurity (probably an iron atom, see section 5.1). Imaging parameters: $31 \times 29 \text{ nm}^2$, 1.2 V, 0.2 nA, 79 K, 90 L

altered star-like features are marked by an orange frame, and the extra bright ones by a purple box. The grid in Figure 5.25 is again to indicate the substrate's lattice and is to study where the new features are centered relative to the lattice positions on the surface. While the altered star-like feature is still sitting on the five-fold coordinated titanium surface atom, the new bright species span over the whole "mini terrace" of the sawtooth, covering the two-fold coordinated oxygen and the five-fold titanium atoms. In order to get some information about the stability with respect to temperature of all those species found after oxygen exposure of the surface, they were counted and the total sum at each specified temperature is shown in Figure 5.26. The graph indicates that the total number of features drops at temperatures higher than 500 K, and that the coverage for oxygen dosing on the TiO₂ anatase (101) surface is two to three percent of a monolayer.

The next step was a combined experiment to test whether the molecular oxygen adsorbed at the surface binds to oxygen defects on the TiO_2 anatase (101) surface. Therefore the



(a) Position of the double spot features on the TiO_2 (b) Position of the star-like features on the anatase (101) surface; 1.2 V, 0.2 nA, 79 K

 TiO_2 anatase (101) surface; 1.2 V, $0.2 \, nA, 79 \, K$

Figure 5.24: Magnification of the two dominant defects observed on the oxygen dosed TiO_2 anatase (101) surface. The grid in the two images is to indicate the position of the observed features relative to the TiO_2 anatase (101) surface.

clean, as prepared TiO_2 anatase (101) surface was cooled to 105 K and irradiated with 500 eV electrons. The electron flux and the dose were the same as mentioned in section 5.3.1, to have a well defined and known starting point for the next preparation step. Figure 5.27(a) shows the electron irradiated surface before the oxygen adsorption. After recording these images, the sample was transferred to the preparation chamber by means of a precooled wobblestick and also the manipulator was kept at 105 K all the time. Then 90 L of oxygen were dosed to the sample in the same way as described above. After re-transferring the crystal into the STM while still keeping the temperature at 105 K, more STM images have been recorded. Then the sample was again taken out of the STM by means of a precooled wobblestick, flashed to 200 K, and retransferred for further STM investigation. Some examples are presented in Figure 5.27(b).

Discussion

To analyze the experimental results, DFT results of our collaboration (A. Selloni, U. Aschauer, Princton University) were used. It was already expected that – similar to the TiO_2 rutile (110) surface – oxygen only weakly adsorbs on the clean surface [101, 102]. In contrast to this, in the presence of subsurface oxygen vacancies, the oxygen molecules prefer the five-fold coordinated titanium site on the surface closest to the subsurface vacancy. Based on (unpublished) DFT results, our collaborators also predicted the following scenario: The extra electronic charge, stemming from the defect, localizes on the adsorbed oxygen molecule, converting it into a superoxide (O_2^-) , which is stable on the TiO₂ anatase (101) surface. If there is enough free charge in the surroundings of the adsorbed molecule



(a) The oxygen dosed TiO_2 anatase (101) surface after heating; $34 \times 34 \text{ nm}^2$, 1.1 V, 0.25 nA, 82 K

(b) Magnification of the new features from Figure 5.25(a) with grid to indicate the position

Figure 5.25: New features on the TiO_2 anatase (101) surface after heating. The boxes are using the same color code as used in Figure 5.23. In addition to this the orange box marks a new altered star-like feature and the purple box indicates a new extra bright species on the TiO_2 anatase (101) surface.

and if the oxygen concentration is low, it can gather more electrons and transform to a peroxide $(O_2^{2^-})$ species (see reference [67]). This peroxide can, as a consequence, induce substantial relaxations, which lead to an energetically more favorable configuration. First principle molecular dynamics (FPMD) calculations performed for a temperature of 220 K showed that a cascade of events could take place in the topmost layers of the TiO₂ anatase (101) crystal. In the first step the subsurface oxygen atom closest to the subsurface vacancy is strongly relaxed towards the surface, while upon the adsorption of the peroxide it returns to its former lattice site. Then one of the oxygen atoms from the bottom of the first TiO₂ layer diffuses into the subsurface vacancy, resulting in an oxygen vacancy in an unstable position (see section 2.2.1 and reference [19]). Finally there is a combined event taking place, where the vacancy is migrating to the position of a two-fold coordinated oxygen atom on the top of the sawtooth and is filled there by the adsorbed oxygen molecule. This whole cascade of events yields a healed subsurface vacancy on the one hand, while on the other it also leads to the incorporation of an oxygen molecule into the surface, which undergoes a transition from a reduced into an oxidized state.

The resulting oxygen molecule at the position of a regular, two-fold coordinated lattice



Figure 5.26: Total coverage of oxygen adsorption related features on the TiO_2 anatase (101) surface after heating the sample to the specified temperature for 10 minutes



(a) Imaging parameters: $29 \times 29 nm^2$, 1.5 V, 0.25 nA, 78 K

(b) Imaging parameters: $29 \times 29 nm^2$, 1.1 V, 0.25 nA, 82 K

(c) Imaging parameters: $29 \times 29 nm^2$, 1.9 V, 0.25 nA, 78 K



oxygen atom could not conclusively be identified in this work. The proof for such a species, namely the adsorption of molecular oxygen on surface oxygen vacancies created by electron bombardment (see Figure 5.27) remained inconclusive. In later experiments performed by a other members of our group the "star-like" feature was identified as an oxygen molecule adsorbed on a five-fold coordinated titanium atom.

The new features, which have been observed in STM images recorded after heating the sample to 500 K for ten minutes are interpreted as the altered star-like features, because their number drops, while the number of features marked with an orange box in Figure

5.25 increases.

Figure 5.23 shows a large number of double features on the oxygen exposed TiO₂ anatase (101) surface indicated by a red box, which are also magnified in Figure 5.24(a). They are unevenly spread over the surface and their number is comparable to the number of dark defects (see black box in Figure 5.23). This indicates that this feature is the image of an oxygen molecule adsorbed on an impurity atom in the surface. If the assumption made in the previous section 5.2 is correct, these impurities could be isolated iron impurities in the surface or near-surface region.

The bright features marked with a purple box in Figure 5.25 can be interpreted as a precursor of the reoxidation process of the surface at this temperature, which could possibly lead to the rough structure shown in Figure 5.2 as an intermediate state. These features could be the product of a titanium interstitial atom attracted to the surface by the distortion of the electronic structure on the TiO₂ anatase (101) surface due to the adsorbed oxygen molecule. In the end, the adsorbed O₂ molecule and the former interstitial titanium atom could form an anatase-like structure.

The experiments mentioned above were all performed for an oxygen dose of 90 L of oxygen. If the dose is increased the total surface coverage turned out to be approximately $(2.5 \pm 1\%)$ of a monolayer. The relatively large error comes form the fact that it was only possible to determine the total coverage from a few STM images, which show only a tiny spot of the sample and therefore the statistical distribution is large. On the other hand, the more precise way of determining the coverage would have been recording LEIS spectra, but it was impossible to obtain useful data due to focussing problems related to the sample's small size. The tiny area of the sample resulted in a bad signal to noise ratio, because of the low countrate. A second problem was the contraction of the manipulator due to the temperature difference and the resulting readjusting of the sample prior to each LEIS experiment.

At this point it should be mentioned that oxygen dosing was always done using the same set of parameters. That means an oxygen gas pressure in the chamber of 10^{-9} mbar for two minutes at a temperature of 105 K without pumping the chamber using the ion pump. When the ion pump was switched on during dosing, via an exchange reaction the ion pump could degas CO, which sticks to the TiO₂ anatase (101) surface. Nevertheless, it was found out that after dosing the sample had to be annealed to a temperature higher than 150 K to get rid of co-adsorbed CO, which came from the inner chamber walls due to an exchange reaction with oxygen. This step was absolutely necessary because, as mentioned in section 5.2.1, the sticking coefficient of CO is higher by a factor of approximately 5000.

The quality of the images shown in Figure 5.27 is not so nice, which is most probably caused by co-adsorbed CO from the inner walls of the preparation chamber. Due to exchange reactions of oxygen and CO on the chamber walls, CO can also adsorb on the sample and due to the much higher sticking coefficient (see section 5.2.1) in comparison to an oxygen molecule, a CO molecule is more likely to stick to the sample. In order to avoid the influence of CO the sample was heated to 195 K to desorb any co-adsorbed CO. In case of oxygen dosing to the clean sample, this treatment was helpful (see section 5.3.2), but unfortunately not in this case.

Chapter 6 Summary

In this dissertation, low-temperature STM was used to study defects on TiO_2 rutile (110) and anatase (101) surfaces, and the defect related adsorption of oxygen. Usually, when the TiO_2 rutile (110) surface is freshly prepared, it contains, depending on its grade of reduction, a certain number of bridging oxygen vacancies. In general, these are equally spread over the surface. The clean TiO_2 rutile (110) surface, containing 0.17 ML of surface oxygen molecules, was exposed to molecular oxygen at 105 K. It had already been known that at this temperature oxygen adsorbs molecularly on the rutile surface, but no direct observation of the adsorbed molecule had been published. In this thesis STM images of adsorbed oxygen are presented. On the dark bridging oxygen rows of the TiO₂ rutile (110) surface the oxygen molecule is only visible as a very faint contrast feature in STM images. This feature is only metastable but could be imaged at low temperature (17 K)using "gentle" tunneling conditions. A gap voltage of 1.3 V and a tunneling current lower than 0.05 nA turned out to be the ideal parameters for the LT-STM setup. This metastable adsorption configuration is easily disturbed by the electric field of the STM tip, which leads to the dissociation of the molecule. The dissociation process occurs via an intermediate step that was recorded in time-lapse STM images: a configuration of oxygen adatoms on neighboring five-fold titanium rows with a bridging oxygen vacancy in between them was found. Again, this intermediate configuration could only be observed for the most gentle tunneling conditions. Scanning with harsher parameters or at higher temperature (e.g., 78 K) leads to an immediate dissociation of the adsorbed oxygen molecules. The intermediate state could be imaged in rare cases, indicating that the same dissociation process is taking place. In a different series of experiments it was confirmed that the STM tip is inducing the dissociation of adsorbed oxygen molecules and that this effect is highly localized.

It was also tried to find a new species – tetraoxygen – adsorbed on the TiO_2 rutile (110) surface. But no evidence was found in STM. In a preliminary UV desorption experiment this species could not be detected either.

In a short STM study it was shown that a small area of a perfect TiO_2 rutile (110) surface can be produced by scanning the area once at high sample bias (5 V) at 77 K. Another series of experiments was performed to test the stability of the formed oxygen adatoms. It could be confirmed that the latter are still present on the TiO_2 rutile (110) surface after heating it to 400 K. A short study using a pulsed laser revealed that laser pulses with a power higher than 20 mJ per pulse at 355 nm wavelength can desorb oxygen adatoms from the TiO_2 rutile (110) surface.

Finally a short adsorption study of carbon monoxide on the TiO_2 rutile (110) surface was performed. It was observed that the CO molecules preferentially adsorb on the five-fold titanium atoms, which is in good agreement with literature (see e.g., [55, 105, 106]). Even low doses of CO almost form a full monolayer on the TiO_2 rutile (110) surface. The presence of bridging oxygen vacancies is not necessary for the CO adsorption, as it is for the adsorption of oxygen.

Compared to the well-known TiO₂ rutile (110) system, less is known about the TiO₂ anatase (101) surface. In a first step, surface preparation parameters had to be established. When the TiO₂ anatase (101) crystal was freshly cleaved ex-situ, a high-quality surface could easily be prepared. After a few sputtering / annealing cycles an almost perfect surface was achieved. Due to the numerous preparation cycles the crystal became reduced and the terrace size became smaller. Therefore the sample was periodically reoxidized. Sometimes after performing the reoxidation a rough structure covering almost the whole TiO₂ anatase (101) surface was observed in STM images. It was found that performing several UHV annealing cycles could reduce the areas covered by this unknown structure and a clean TiO₂ anatase (101) surface could be reestablished.

After finding the optimal preparation parameters for a clean TiO_2 anatase (101) surface a series of experiments was performed to experimentally test predictions made by theorists. According to DFT calculations oxygen vacancies are more stable in the bulk than on the surface of TiO_2 anatase (101). An electron gun was used to desorb two-fold coordinated oxygen atoms from the surface at 105 K. After creation of these surface vacancies their stability at different temperatures was investigated. It turned out that there exists a dynamic equilibrium concentration of surface oxygen vacancies for each temperature. An analysis showed that, once this equilibrium is established, the number of surface oxygen defects on the TiO_2 anatase (101) surface stays constant. If the electron irradiated sample is heated to a temperature of 200 K the surface vacancies start migrating subsurface and their total number decreases. Recording series of time-lapse STM images at temperatures in the range between 223 and 300 K revealed that the equilibrium concentration of surface oxygen vacancies is a dynamic one and that the latter are migrating subsurface and back to the surface, with the overall number remaining almost constant. At a temperature of 450 K most of the oxygen vacancies have migrated subsurface. During this series of experiments a new feature, spanning over more than one surface unit cell, was observed in the temperature interval between 300 and 450 K. The large extension of this feature, which is often different in size, indicates that it is probably located in the subsurface layer and that it modifies the local electronic structure.

In a different series of experiments the adsorption of oxygen on the clean TiO_2 anatase (101) surface was tested at 105 K. It turned out to be necessary to first check the adsorption of carbon monoxide. When oxygen is dosed into the UHV system it replaces CO molecules at the inner walls of the chamber. Due to the high sticking probability of CO on the

TiO₂ anatase (101) surface this was disturbing the oxygen adsorption study. It was found that CO, which is adsorbed at the surface at 105 K, is weakly bound and its desorption starts at a temperature of 120 K. At temperatures higher than 150 K no CO was observed in STM images. At 105 K oxygen adsorbs on the TiO₂ anatase (101) surface in different configurations. STM images recorded after oxygen exposure and heating the sample to 200 K to remove the co-adsorbed CO show star-like features, bright double features and bright double or triple features surrounded by a dark halo. When the sample was heated higher than 325 K the number of double features remained constant, while a decrease of the number of star-like features was observed and a new, bright species appeared. This new bright features possibly are precursors of the reoxidation process of the reduced bulk. Additionally, a combined experiment of electron bombarded and oxygen exposed TiO₂ anatase (101) surface was done. First, surface oxygen vacancies were created via electron bombardment and in the second step oxygen was dosed to the surface. Unfortunately it was almost impossible to record STM images on this surface.

Chapter 7 Appendix

7.1 Tables

The listed STM images are all stored in the LT-STM lab on the Sun STM computer.

Figure	Folder	File
2.2	TiO2_110	(a) m1066
		(b) m1096
2.3	TiO2_110	m1490
4.13	TiO2_110n3	m1812
2.7	Anatase_101	(a) m1704
		(b) m1759
2.9	Anatase_101	(a) m1193
		(b) m2792
4.2	TiO2_110n3	(a) m2297
4.3	TiO2_110	(a) m1419
		(b) m1427
4.4	TiO2_110	1429
4.5	TiO2_110n3	(a) m2088
		(b) m2088
4.6	TiO2_110n3	(a) m2093
4.7	TiO2_110n3	(a) m2088
		(b) $m2254$
4.8	TiO2_110n3	(a) m2093
		(b) m2094
		(c) m2095
		(d) m2097
4.9	$TiO2_{110n3}$	(a) m2277
		(b) m2286

Figure	Folder	File
4.10	TiO2_110n3	(a) m1763
	_	(b) m1764
4.11	TiO2_110n3	(a) m2230
		(b) m2231
4.13	TiO2_110n3	m1812
4.14	TiO2_110n3	(a) m2034
		(b) $m2035$
5.2	Anatase_101	(a) m3135
5.3	Anatase_101-2	(a) m4027
		(b) m4028
		(c) $m4029$
		(d) m4030
5.7	Anatase_101	m2118
		inset $m1757$
		inset m1758
		inset $m1759$
		inset m1760
		inset m1761
5.8	Anatase_101-2	m3927
5.9	Anatase_101-2	m4380
5.10	Anatase_101-2	m4380
5.12	Anatase_101	m2339
5.13 (b)	Anatase_101	m2339
5.16	Anatase_101	m2037
5.17	Anatase_101-2	m3010
		m3012
		m3014
		m3016
		m3019
		m3021
		m3023
		m3025
		m3027
		m3029
	A	m3031
5.20	Anatase_101-2	m3654
5.23	Anatase_101-2	m3889
5.24	Anatase_101-2	(a) m3889
	A	(b) m3889
5.25	Anatase_101-2	(a) m4010
		(b) m4010

Figure	Folder	File
5.27	Anatase_101-2	(a) m4271
		(b) $m4275$
		(c) m4298

Table A 1: List of STM images

Image	Temperature (K)	Time (s)	Defects (ML)
2410	301	0	0.036828002
2411	301	180	0.037319042
2412	301	360	0.040265283
2413	301	540	0.039774243
2414	301	660	0.037810082
2415	301	840	0.036828002
2416	301	1020	0.035845922
2417	301	1200	0.036336962
2418	301	1320	0.034863842
2420	301	1500	0.035845922
2422	301	0	0.024375659
2423	301	240	0.026148434
2424	301	420	0.024375659
2425	301	600	0.027478016
2426	301	780	0.026148434
2427	301	960	0.026591628
2428	301	1080	0.025262047
2429	301	1320	0.025705241
2430	301	1560	0.026591628
2431	301	1800	0.024818853
2432	301	2040	0.027478016
2433	301	2220	0.026148434
2434	301	2460	0.026148434
2435	301	2700	0.026591628
2436	301	2940	0.026148434
2437	301	3240	0.022602884
2438	301	3480	0.023932465
2446	266	0	0.087051406
2447	266	240	0.087051406
2448	266	480	0.085036327
2449	266	720	0.087051406

Image	Temperature (K)	Time (s)	Defects (ML)
2450	266	960	0.082215217
2451	266	1200	0.088260453
2452	266	1380	0.080603154
2453	266	0	0.086415651
2454	266	300	0.082116365
2455	266	540	0.080826579
2456	266	780	0.081686436
2457	266	1020	0.079966722
2458	266	1260	0.080826579
2460	266	1740	0.087705437
2461	266	2040	0.087275508
2462	266	2280	0.081256508
2463	266	2580	0.085125865
2520	246	0	0.176411828
2521	246	360	0.180760007
2522	246	600	0.180760007
2523	246	960	0.17206365
2524	246	1260	0.184487018
2525	246	1620	0.174548323
2526	246	0	0.202790305
2527	246	180	0.202790305
2528	246	360	0.197961964
2529	246	600	0.202790305
2530	246	1020	0.197961964
2531	246	1260	0.202790305
2532	246	1500	0.202790305
2533	246	1740	0.212446986
2534	246	1980	0.222103667
2535	246	2460	0.226932008
2536	246	2700	0.231760349
2537	246	2880	0.226932008
2538	246	3180	0.212446986
2539	246	3420	0.207618646
2540	246	3660	$0.2027903\overline{05}$
2541	246	3840	0.202790305
2542	246	4380	$0.23184\overline{6093}$
2543	246	4860	$0.23184\overline{6093}$

Image	Temperature (K)	Time (s)	Defects (ML)
2544	246	5340	0.231846093
2563	256	0	0.132855821
2564	256	300	0.130483395
2565	256	660	0.131432366
2566	256	840	0.135702731
2567	256	1080	0.133804791
2568	256	1260	0.134753761
2569	256	1500	0.134279276
2570	256	1740	0.134753761
2571	256	1980	0.135702731
2572	256	2160	0.134279276
2575	256	0	0.137816012
2576	256	300	0.135959904
2577	256	600	0.136887958
2578	256	900	0.138280039
2579	256	1200	0.134567823
2580	256	1440	0.140600174
2599	223	0	0.193918985
2601	223	240	0.188770694
2602	223	360	0.187054596
2603	223	540	0.194777034
2686	295	0	0.030446917
2687	295	300	0.028272138
2688	295	540	0.030011961
2689	295	780	0.028272138
2690	295	1020	0.027837182
2691	295	1260	0.027837182
2007	77	0	0.323432971
2008	77	240	0.323432971
2009	77	420	0.323432971
2010	77	600	0.323432971
2011	77	780	0.323432971

Table A 2: Raw data of the time stability of surface oxygen defects on the TiO_2 anatase (101) surface presented in Figure 5.15 in the main text.

Image	Measured	Calibrated	Area	# Defects	$\# \ \mathbf{Jumps}$	Jumps	Temperature
	$area (nm^2)$	area (nm^2)	calibration		(ML)	(ML)	(K)
2410	1220	1578.47	0.7729	75	0	0.2538	301
2411	1220	1578.47	0.7729	76	18	0.5074	301
2412	1220	1578.47	0.7729	82	32	0.5072	301
2413	1220	1578.47	0.7729	81	34	0.5070	301
2414	1220	1578.47	0.7729	77	24	0.5068	301
2415	1220	1578.47	0.7729	75	20	0.5066	301
2416	1220	1578.47	0.7729	73	12	0.5064	301
2417	1220	1578.47	0.7729	74	24	0.5062	301
2418	1220	1578.47	0.7729	71	18	0.5060	301
2420	1220	1578.47	0.7729	73	12	0.5056	301
2421	1220	1578.47	0.7729	65	26	0.5054	301
2422	1365	1748.88	0.7805	55	0	0.5597	301
2423	1365	1748.88	0.7805	59	40	0.5594	301
2424	1365	1748.88	0.7805	55	24	0.5592	301
2425	1365	1748.88	0.7805	62	42	0.5590	301
2426	1365	1748.88	0.7805	59	36	0.5588	301
2427	1365	1748.88	0.7805	60	48	0.5585	301
2428	1365	1748.88	0.7805	57	42	0.5583	301
2429	1365	1748.88	0.7805	58	44	0.5581	301
2430	1365	1748.88	0.7805	60	58	0.5578	301
2431	1365	1748.88	0.7805	56	74	0.5576	301
2432	1365	1748.88	0.7805	62	44	0.5574	301
2433	1365	1748.88	0.7805	59	64	0.5571	301
2434	1365	1748.88	0.7805	59	56	0.5569	301
2435	$1\overline{365}$	1748.88	0.7805	60	44	0.5567	301
2436	1365	1748.88	0.7805	59	72	0.5565	301
2437	1365	1748.88	0.7805	51	48	0.5562	301
2438	1365	1748.88	0.7805	54	30	0.5560	301

Image	Measured	Calibrated	Area	# Defects	# Jumps	Jumps	Temperature
	area (nm^2)	area (nm^2)	calibration		(ML)	(ML)	(K)
2446	1443	1923.23	0.7503	216	0	0.6094	266
2447	1443	1923.23	0.7503	216	44	0.6092	266
2448	1443	1923.23	0.7503	211	32	0.6089	266
2449	1443	1923.23	0.7503	216	36	0.6087	266
2450	1443	1923.23	0.7503	204	22	0.6084	266
2451	1443	1923.23	0.7503	219	26	0.6082	266
2452	1443	1923.23	0.7503	200	12	0.6079	266
2453	1346	1802.84	0.7466	201	0	0.5697	266
2454	1346	1802.84	0.7466	191	20	0.5694	266
2455	1346	1802.84	0.7466	188	20	0.5692	266
2456	1346	1802.84	0.7466	190	20	0.5690	266
2457	1346	1802.84	0.7466	186	30	0.5687	266
2458	1346	1802.84	0.7466	188	20	0.5685	266
2460	1346	1802.84	0.7466	204	22	0.5680	266
2461	1346	1802.84	0.7466	203	30	0.5678	266
2462	1346	1802.84	0.7466	189	24	0.5676	266
2463	1346	1802.84	0.7466	198	40	0.5673	266
2520	1133	1247.80	0.908	284	0	0.3838	246
2521	1133	1247.80	0.908	291	0	0.3836	246
2522	1133	1247.80	0.908	291	42	0.3835	246
2523	1133	1247.80	0.908	277	22	0.3833	246
2524	1133	1247.80	0.908	297	10	0.3832	246
2525	1133	1247.80	0.908	281	16	0.3830	246
2526	160	160.53	0.9967	42	0	0.0493	246
2527	160	160.53	0.9967	42	6	0.0492	246
2528	160	160.53	0.9967	41	6	0.0492	246
2529	160	160.53	0.9967	42	6	0.0492	246
2530	160	160.53	0.9967	41	6	0.0492	246

Image	Measured	Calibrated	Area	# Defects	# Jumps	Jumps	Temperature
	$area (nm^2)$	area (nm^2)	calibration		(ML)	(ML)	(K)
2531	160	160.53	0.9967	42	2	0.0492	246
2532	160	160.53	0.9967	42	8	0.0491	246
2533	160	160.53	0.9967	44	8	0.0491	246
2534	160	160.53	0.9967	46	6	0.0491	246
2535	160	160.53	0.9967	47	4	0.0491	246
2536	160	160.53	0.9967	48	0	0.0491	246
2537	160	160.53	0.9967	47	2	0.0490	246
2538	160	160.53	0.9967	44	0	0.0490	246
2539	160	160.53	0.9967	43	4	0.0490	246
2540	160	160.53	0.9967	42	0	0.0490	246
2541	160	160.53	0.9967	42	8	0.0490	246
2542	160	137.07	1.1673	41	4	0.0418	246
2543	160	137.07	1.1673	41	0	0.0418	246
2544	160	137.07	1.1673	41	2	0.0418	246
2563	1085	1633.54	0.6642	280	0	0.4940	256
2564	1085	1633.54	0.6642	275	32	0.4938	256
2565	1085	1633.54	0.6642	277	12	0.4936	256
2566	1085	1633.54	0.6642	286	4	0.4934	256
2567	1085	1633.54	0.6642	282	24	0.4932	256
2568	1085	1633.54	0.6642	284	4	0.4930	256
2569	1085	1633.54	0.6642	283	12	0.4929	256
2570	1085	1633.54	0.6642	284	8	0.4927	256
2571	1085	1633.54	0.6642	286	8	0.4925	256
2572	1085	1633.54	0.6642	283	12	0.4923	256
2575	1432	1670.36	0.8573	297	0	0.5028	256
2576	1432	1670.36	0.8573	293	2	0.5026	256
2577	1432	1670.36	0.8573	295	34	0.5024	256
2578	1432	$1\overline{670.36}$	0.8573	298	34	0.5022	256

Image	Measured	Calibrated	Area	# Defects	# Jumps	Jumps	Temperature
	$area (nm^2)$	$area (nm^2)$	$\operatorname{calibration}$		(ML)	(ML)	(K)
2579	1432	1670.36	0.8573	290	20	0.5020	256
2580	1432	1670.36	0.8573	303	24	0.5018	256
2599	868	903.32	0.9609	226	0	0.2694	223
2601	868	903.32	0.9609	220	2	0.2692	223
2602	868	903.32	0.9609	218	14	0.2691	223
2603	868	903.32	0.9609	227	14	0.2690	223
2686	1200	1782.00	0.6734	70	0	0.5142	295
2687	1200	1782.00	0.6734	65	12	0.5140	295
2688	1200	1782.00	0.6734	69	20	0.5138	295
2689	1200	1782.00	0.6734	65	10	0.5137	295
2690	1200	1782.00	0.6734	64	28	0.5135	295
2691	1200	1782.00	0.6734	64	40	0.5133	295

Table A 3: Raw data of the defect migration on the TiO_2 anatase (101) surface after electron bombardment presented in Figure 5.18 in the main text.

Image	Measured	Calibrated	Area	# CO	CO (ML)	Unit cells	Treatment
	area (nm^2)	area (nm^2)	calibration			per image	
4343	100	162.63	0.6149	179	0.4266	419.6354	0.03 L
4344	625	1046.38	0.5973	950	0.3519	2700.0019	0.03 L
4345	420	553.14	0.7593	709	0.4967	1427.2908	0.03 L
4349	100	131.80	0.7587	110	0.3234	340.0999	0.03 L
4350	98	171.60	0.5711	157	0.3546	442.7825	0.03 L
4351	547	853.62	0.6408	811	0.3682	2202.6292	0.03 L
4352	625	983.63	0.6354	951	0.3747	2538.1038	0.03 L
4353	100	155.21	0.6443	178	0.4445	400.4870	0.03 L
4354	100	155.74	0.6421	167	0.4156	401.8592	0.03 L
4355	98	157.86	0.6208	161	0.3953	407.3343	0.03 L
4356	625	1084.13	0.5765	0	0.0000	2797.4174	200 K

Image	Measured	Calibrated	Area	# CO	CO (ML)	Unit cells	Treatment
	area (nm^2)	area (nm^2)	calibration			per image	
4368	288	499.31	0.5768	358	0.2779	1288.3795	$0.02\mathrm{L}$
4369	100	206.57	0.4841	175	0.3283	533.0175	0.02 L
4371	625	1148.90	0.5440	817	0.2756	2964.5426	0.02L
4372	100	192.90	0.5184	119	0.2391	497.7504	0.02 L
4373	100	197.01	0.5076	135	0.2656	508.3408	0.02 L
4374	100	176.87	0.5654	109	0.2388	456.3739	0.02 L
4378	100	152.67	0.6550	97	0.2462	393.9447	0.02 L
4379	100	151.88	0.6584	99	0.2526	391.9104	0.02 L
4380	100	149.59	0.6685	107	0.2772	385.9892	0.02 L
4381	100	151.45	0.6603	2	0.0051	390.7827	150 K
4382	100	163.05	0.6133	0	0.0000	420.7301	150 K
4383	100	159.29	0.6278	2	0.0049	411.0127	150 K
4384	625	1042.36	0.5996	1	0.0004	2689.6450	150 K
4385	625	1000.00	0.6250	1	0.0004	2580.3379	150 K
4386	100	280.90	0.3560	153	0.2111	724.8140	$0.04\mathrm{L}$
4387	100	128.14	0.7804	149	0.4506	330.6430	$0.04\mathrm{L}$
4388	100	121.11	0.8257	163	0.5216	312.5031	0.04 L
4389	100	131.30	0.7616	158	0.4663	338.8049	0.04 L
4390	100	114.12	0.8763	151	0.5128	294.4583	0.04 L
4391	100	144.34	0.6928	135	0.3625	372.4506	0.04 L
4392	100	123.17	0.8119	149	0.4688	317.8147	$0.04\mathrm{L}$
4393	100	138.62	0.7214	132	0.3690	357.6848	0.04 L
4394	625	1036.66	0.6029	1008	0.3768	2674.9231	0.04 L
4395	625	944.11	0.6620	862	0.3538	2436.1196	0.04 L
4396	625	$10\overline{10.35}$	0.6186	1144	0.4388	$26\overline{07.0339}$	0.04 L
4397	625	914.54	0.6834	1066	0.4517	2359.8349	0.04 L
4398	625	947.83	0.6594	118	0.0482	$2445.725\overline{1}$	130 K
4399	625	897.09	0.6967	115	0.0497	$2314.785\overline{6}$	130 K

Image	Measured	Calibrated	Area	# CO	CO (ML)	Unit cells	Treatment
	area (nm^2)	area (nm^2)	calibration			per image	
4400	625	938.16	0.6662	117	0.0483	2420.7613	130 K
4401	100	136.82	0.7309	17	0.0482	353.0357	130 K
4404	625	864.10	0.7233	1076	0.4826	2229.6573	0.04 L
4405	625	815.71	0.7662	1103	0.5240	2104.8175	0.04 L
4406	100	134.68	0.7425	184	0.5295	347.5202	0.04 L
4407	100	132.70	0.7536	195	0.5695	342.4015	0.04 L
4408	625	896.70	0.6970	1046	0.4521	2313.7893	0.04 L
4409	100	160.46	0.6232	187	0.4516	414.0465	0.04 L
4410	100	159.26	0.6279	153	0.3723	410.9473	0.04 L
4411	100	122.38	0.8171	138	0.4370	315.7922	0.04 L
4412	100	135.67	0.7371	123	0.3514	350.0662	120 K
4413	100	131.91	0.7581	121	0.3555	340.3691	120 K
4414	100	124.19	0.8052	115	0.3589	320.4592	120 K
4419	353	494.61	0.7137	412	0.3228	1276.2495	0.02L
4423	625	1015.27	0.6156	929	0.3546	2619.7387	0.02L
4424	625	1029.15	0.6073	1010	0.3803	2655.5428	0.02L
4426	625	1072.96	0.5825	896	0.3236	2768.6028	0.02L
4427	625	1045.68	0.5977	878	0.3254	2698.1950	0.02 L
4428	100	169.61	0.5896	138	0.3153	437.6421	0.02 L
4429	100	168.95	0.5919	157	0.3601	435.9415	$0.02\mathrm{L}$
4430	100	170.68	0.5859	162	0.3678	440.4058	0.02L
4431	625	1066.73	0.5859	934	0.3393	$2\overline{752.5365}$	109 K
4432	625	1066.73	0.5859	948	0.3444	2752.5365	109 K
4433	100	170.68	0.5859	156	0.3542	440.4058	109 K
4434	100	170.42	0.5868	148	0.3366	439.7304	109 K

Table A 4: Raw data for CO adsorption on the TiO_2 anatase (101) surface (coverage vs temperature measurements) presented in Figure 5.11 in the main text.

Image	Measured	Calibrated	Area	$\# \mathbf{O}_2$	Doubles	$\# \mathbf{O}_2$	Stars	O_2	O_2 total	Treatment
	area (nm^2)	area (nm^2)	calibr.	double	(ML)	\mathbf{star}	(ML)	Total	(ML)	
3729	300	500.92	0.5989							dosing
3731	196	310.27	0.6317							dosing
3743	866	1240.69	0.6980	57	0.0089	42	0.0066	104	0.0162	10 Min. 153K
3745	288	406.38	0.7087	34	0.0162	29	0.0138	64	0.0305	10 Min. 153K
3748	584	949.13	0.6153	33	0.0067	50	0.0102	87	0.0178	10 Min. 153K
3753	352	599.25	0.5874		0.0000		0.0000	2400	0.7761	dosing
3756	660	952.66	0.6928		0.0000		0.0000			dosing
3759	552	843.78	0.6542		0.0000		0.0000			dosing
3761	225	330.54	0.6807		0.0000		0.0000			dosing
3765	480	769.72	0.6236	34	0.0086	29	0.0073	64	0.0161	10 Min. 200K
3766	225	381.36	0.5900	33	0.0168	22	0.0112	56	0.0285	10 Min. 200K
3767	206	350.64	0.5875	15	0.0083	15	0.0083	30	0.0166	10 Min. 200K
3769	476	793.07	0.6002	44	0.0108	27	0.0066	73	0.0178	10 Min. 200K
3786	1024	1770.71	0.5783		0.0000		0.0000	1900	0.2079	dosing
3788	644	1051.09	0.6127		0.0000		0.0000	1160	0.2139	dosing
3794	316	514.83	0.6138	67	0.0252	65	0.0245	134	0.0504	10 Min. 132K
3797	408	708.09	0.5762	69	0.0189	85	0.0233	156	0.0427	10 Min. 132K
3803	792	1420.88	0.5574		0.0000		0.0000	740	0.1009	dosing
3804	376	557.28	0.6747		0.0000		0.0000	309	0.1074	dosing
3810	396	695.35	0.5695		0.0000		0.0000	400	0.1115	dosing
3814	684	1272.56	0.5375		0.0000		0.0000	245	0.0373	10 Min. $275 {\rm \dot{K}}$
3816	291	474.17	0.6137	64	0.0262	12	0.0049	78	0.0319	10 Min. 275K
3817	466	759.33	0.6137	62	0.0158	24	0.0061	89	0.0227	10 Min. 275K
3824	1300	2204.88	0.5896		0.0000		0.0000	474	0.0417	dosing
3834	347	591.44	0.5867	18	0.0059	10	0.0033	29	0.0095	10 Min. 176K
3878	188	294.16	0.6391	25	0.0165	11	0.0072	36	0.0237	dosing
3882	665	1126.74	0.5902	105	0.0181	39	0.0067	148	0.0255	dosing
3885	288	482.09	0.5974	58	0.0233	31	0.0125	92	0.0370	dosing

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Image	Measured	Calibrated	Area	$\# \mathbf{O}_2$	Doubles	$\# \mathbf{O}_2$	Stars	\mathbf{O}_2	O_2 total	Treatment
	area (nm^2)	area (nm^2)	calibr.	double	(ML)	\mathbf{star}	(ML)	Total	(ML)	
3886	188	309.92	0.6066	34	0.0213	14	0.0088	48	0.0300	dosing
3889	527	820.87	0.6420	88	0.0208	24	0.0057	114	0.0269	10 Min. 194 $\dot{\mathrm{K}}$
3890	340	522.43	0.6508	53	0.0197	18	0.0067	73	0.0271	10 Min. 194K
3891	1080	1631.91	0.6618	179	0.0213	46	0.0055	229	0.0272	10 Min. 194K
3900	616	1102.76	0.5586	46	0.0081	79	0.0139	127	0.0223	dosing
3902	59	104.55	0.5643	7	0.0130	6	0.0111	15	0.0278	dosing
3904	636	1086.25	0.5855	101	0.0180	45	0.0080	148	0.0264	dosing
3906	416	658.23	0.6320	36	0.0106	29	0.0085	68	0.0200	dosing
3909	1188	2179.82	0.5450	129	0.0115	42	0.0037	199	0.0177	10 Min. $354 {\rm \dot{K}}$
3910	625	1070.76	0.5837	40	0.0072	52	0.0094	109	0.0197	10 Min. 354K
3911	225	392.81	0.5728	14	0.0069	19	0.0094	46	0.0227	10 Min. 354K
3964	1012	1676.05	0.6038	87	0.0101	111	0.0128	200	0.0231	dosing
3965	625	970.35	0.6441	36	0.0072	68	0.0136	106	0.0212	dosing
3967	1200	1888.57	0.6354	70	0.0072	56	0.0057	127	0.0130	dosing
3969	932	1572.20	0.5928	102	0.0126	45	0.0055	168	0.0207	dosing
3971	1600	2767.69	0.5781		0.0000	67	0.0047	200	0.0140	10 Min. 420K
3972	625	1089.61	0.5736		0.0000	36	0.0064	109	0.0194	10 Min. 420K
3974	120	220.79	0.5435		0.0000	4	0.0035	13	0.0114	10 Min. 420K
3976	333	504.47	0.6601		0.0000	17	0.0065	55	0.0211	10 Min. 420K
3977	136	222.19	0.6121		0.0000	8	0.0070	30	0.0262	10 Min. 420K
3978	225	375.94	0.5985		0.0000	8	0.0041	37	0.0191	10 Min. 420K
3979	225	370.07	0.6080		0.0000	11	0.0058	40	0.0209	10 Min. 420K
3997	672	1177.71	0.5706	208	0.0342	17	0.0028	230	0.0378	dosing
3998	256	440.24	0.5815	73	0.0321	17	0.0075	95	0.0418	dosing
4002	200	328.84	0.6082	53	0.0312	13	0.0077	70	0.0412	dosing
4005	1172	2111.71	0.5550		0.0000	118	0.0108	314	0.0288	10 Min. 492K
4008	736	1262.44	0.5830		0.0000	30	0.0046	223	0.0342	10 Min. 492K

Image	Measured	Calibrated	Area	$\# \mathbf{O}_2$	Doubles	$\# \mathbf{O}_2$	Stars	\mathbf{O}_2	O_2 total	Treatment
	area (nm^2)	area (nm^2)	calibr.	double	(ML)	star	(ML)	Total	(ML)	
4009	444	715.44	0.6206		0.0000	26	0.0070	91	0.0246	10 Min. 492K
4010	189	308.97	0.6117		0.0000	11	0.0069	52	0.0326	10 Min. 492K
4011	225	362.14	0.6213		0.0000	9	0.0048	54	0.0289	10 Min. 492K
4012	1600	2464.19	0.6493		0.0000	65	0.0051	412	0.0324	10 Min. 492K
4015	108	148.82	0.7257	39	0.0508	4	0.0052	44	0.0573	dosing
4018	176	256.37	0.6865	78	0.0590	5	0.0038	87	0.0658	dosing
4019	600	904.70	0.6632	187	0.0401	13	0.0028	206	0.0441	dosing
4022	1200	2188.58	0.5483		0.0000	32	0.0028	278	0.0246	10 Min. 562K
4023	413	811.87	0.5087		0.0000	19	0.0045	58	0.0138	10 Min. 562K
4024	1248	2098.18	0.5948		0.0000	28	0.0026	184	0.0170	10 Min. 562K
4025	225	420.33	0.5353		0.0000	5	0.0023	50	0.0231	10 Min. 562K
4035	308	535.09	0.5756	90	0.0326	27	0.0098	123	0.0445	dosing
4039	356	566.79	0.6281	58	0.0198	32	0.0109	98	0.0335	dosing
4043	1600	2594.88	0.6166		0.0000	5	0.0004	22	0.0016	10 Min. 653K
4052	1600	2543.32	0.6291	126	0.0096	79	0.0060	214	0.0163	dosing
4055	328	531.95	0.6166	62	0.0226	11	0.0040	77	0.0280	dosing
4060	1600	2550.21	0.6274		0.0000	60	0.0046	144	0.0109	10 Min. 612K
4062	1600	2642.01	0.6056		0.0000	27	0.0020	195	0.0143	10 Min. 612K

Table A 5: Raw data for O_2 adsorption on the TiO_2 anatase (101) surface (coverage vs temperature measurements) presented in Figure 5.26 in the main text.

Image	Measured	Calibrated	Area	# defects	# defects	Treatment
	area (nm^2)	area (nm^2)	calibr.		(ML)	
1931	1344	1961.184883	0.6853	879	0.347395158	e-bombardment
1944	1500	2419.354839	0.62	790	0.253093472	10 Min 280K
1999	1503.91	2209.682633	0.6806	0	0	clean
2001	1448.45	2115.143107	0.6848	0	0	clean

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Image	Measured	Calibrated	Area	# defects	# defects	Treatment
	area (nm^2)	area (nm^2)	calibr.		(ML)	
2002	1550.03	2211.485233	0.7009	904	0.316838398	e-bombardment
2003	1462.65	2001.436782	0.7308	882	0.341570323	e-bombardment
2004	1478.3	1983.23048	0.7454	933	0.36463796	e-bombardment
2005	1468.01	1974.98991	0.7433	881	0.3457518	e-bombardment
2009	216.996	290.9183537	0.7459	162	0.431615782	e-bombardment
2030	1589.24	2240.259374	0.7094	507	0.175413526	10 Min 326K
2035	225	327.1299796	0.6878	84	0.199027167	10 Min 326K
2039	1451.57	2131.840211	0.6809	533	0.193787599	10 Min 326K
2040	1440	2134.914752	0.6745	526	0.190967133	10 Min 326K
2101	1575	2111.260054	0.746	927	0.340323098	e-bombardment
2113	1512	2192.575406	0.6896	841	0.29729998	10 Min 260K
2144	1537	2230.769231	0.689	842	0.292557252	e-bombardment
2150	1544	2350.076104	0.657	414	0.136543754	10 Min 300K
2160	1324	1793.066089	0.7384	573	0.247691867	e-bombardment
2163	1203	1646.366498	0.7307	583	0.274470363	e-bombardment
2169	225	310.2592388	0.7252	112	0.279799364	e-bombardment
2178	1600	2112.211221	0.7575	238	0.087335947	10 Min 350K
2180	1375	1814.462919	0.7578	200	0.085434901	10 Min 350K
2200	1600	2323.89252	0.6885	693	0.23113761	e-bombardment
2211	1204	1735.120334	0.6939	235	0.104976402	10 Min 375 K
2214	1600	2394.492667	0.6682	253	0.081895574	10 Min 375 K
2215	1600	2361.623616	0.6775	315	0.103383991	10 Min 375 K
2217	1600	2343.635565	0.6827	282	0.093263659	10 Min 375 K
2218	225	$3\overline{01.5277406}$	0.7462	36	0.09253982	10 Min 375 K
2219	1339	$19\overline{46.786857}$	0.6878	199	0.079229715	10 Min 375 K
2239	1600	2415.458937	0.6624	744	0.23874083	e-bombardment
2240	1213	$19\overline{44.845278}$	0.6237	514	0.204847885	e-bombardment
2241	1329	1997.89537	0.6652	552	0.214150829	e-bombardment

Image	Measured	Calibrated	Area	# defects	# defects	Treatment
	area (nm^2)	area (nm^2)	calibr.		(ML)	
2242	916	1453.506823	0.6302	398	0.21223618	e-bombardment
2243	976	1633.746234	0.5974	436	0.206849899	e-bombardment
2244	1144	1656.530553	0.6906	476	0.222720875	e-bombardment
2245	225	321.9344685	0.6989	105	0.252798937	e-bombardment
2246	1504	2310.291859	0.651	692	0.232162819	e-bombardment
2249	1036	1556.958221	0.6654	459	0.228501549	e-bombardment
2251	225	357.9952267	0.6285	97	0.210013842	e-bombardment
2253	1294	2016.518622	0.6417	539	0.207176242	10 Min 190K
2254	1600	2308.469196	0.6931	641	0.21522235	10 Min 190K
2255	225	321.2908753	0.7003	95	0.229181014	10 Min 190K
2258	1600	2542.911634	0.6292	660	0.201171331	10 Min 190K
2263	1600	2360.578342	0.6778	653	0.214411555	10 Min 190K
2264	225	324.6284807	0.6931	93	0.222049476	10 Min 190K
2277	1600	2571.520411	0.6222	743	0.223950615	e-bombardment
2278	860	1342.281879	0.6407	351	0.202682761	e-bombardment
2279	225	333.3827234	0.6749	105	0.244117904	e-bombardment
2281	1136	1683.212328	0.6749	495	0.227939567	e-bombardment
2283	225	322.5344037	0.6976	105	0.252328715	e-bombardment
2284	1600	2512.957437	0.6367	756	0.233179349	e-bombardment
2285	225	336.876778	0.6679	116	0.266894938	e-bombardment
2287	225	326.0397044	0.6901	114	0.271011539	e-bombardment
2288	143	236.5200132	0.6046	88	0.288382034	10 Min 300K
2290	743	1201.682031	0.6183	255	0.164476568	10 Min 300K
2292	1255	1958.489388	0.6408	356	0.140890658	10 Min 300K
2320	1600	2329.644729	0.6868	651	0.216593149	e-bombardment
2321	225	307.9239086	0.7307	97	0.244164065	e-bombardment
2324	1600	2220.371912	0.7206	644	0.224808933	10 Min 400K
2326	1600	2220.371912	0.7206	125	0.043635274	10 Min 400K

Image	Measured	Calibrated	Area	# defects	# defects	Treatment
	area (nm^2)	area (nm^2)	calibr.		(ML)	
2335	1457	1944.741057	0.7492	528	0.210438677	e-bombardment
2336	1471	2172.82127	0.677	644	0.229728716	e-bombardment
2337	1420	1979.921919	0.7172	539	0.211005669	e-bombardment
2238	1307	1802.758621	0.725	462	0.198635934	e-bombardment
2339	225	302.9894964	0.7426	97	0.24814046	e-bombardment
2340	965	1417.033774	0.681	354	0.193631711	e-bombardment
2341	1600	2110.817942	0.758	797	0.292658382	e-bombardment
2343	936	1433.603921	0.6529	3	0.00162198	10 Min 450K
2347	1600	2212.69534	0.7231	4	0.001401173	10 Min 450K
3202	1443	2640.922401	0.5464	779	0.228631065	e-bombardment
3203	1600	2855.613064	0.5603	780	0.211713555	e-bombardment
3204	1600	2855.613064	0.5603	772	0.209542134	e-bombardment
3205	1600	2648.129758	0.6042	816	0.238838492	e-bombardment
3207	1600	2706.359946	0.5912	829	0.237422785	e-bombardment
3208	1600	2895.927602	0.5525	822	0.220007527	e-bombardment
3211	168	277.1362587	0.6062	87	0.24332085	e-bombardment
3212	1600	2900.126881	0.5517	858	0.229310379	10 Min 100K
3214	1600	2878.733357	0.5558	885	0.238284204	10 Min 100K
3216	1600	2796.713861	0.5721	820	0.227258031	10 Min 100K
3218	1600	2786.970911	0.5741	836	0.232502306	10 Min 100K
3221	1600	3220.611916	0.4968	830	0.199752912	$10 { m Min} 100 { m K} + 10 { m Min} 162 { m K}$
3223	1600	2610.540055	0.6129	800	0.237527035	$10 { m ~Min} \ 100 { m K} + 10 { m ~Min} \ 162 { m K}$
3224	1600	2573.174654	0.6218	806	0.242783518	$10 { m ~Min} \ 100 { m K} + 10 { m ~Min} \ 162 { m K}$
3225	1600	2761.954083	0.5793	798	0.223944221	$10 { m Min} 100 { m K} + 10 { m Min} 162 { m K}$
3226	1600	2761.954083	0.5793	803	0.22534738	$10 { m Min} 100 { m K} + 10 { m Min} 162 { m K}$
3231	225	384.4182471	0.5853	107	0.215741258	$10 { m ~Min} \ 100 { m K} + 10 { m ~Min} \ 162 { m K}$
3234	1368	2394.538771	0.5713	728	0.23564755	$10 { m Min} 100 { m K} + 10 { m Min} 162 { m K}$
3251	1600	2750.08594	0.5818	761	0.214482476	e-bombardment

Image	Measured	Calibrated	Area	# defects	# defects	Treatment
	area (nm^2)	area (nm^2)	calibr.		(ML)	
3253	1600	2859.185132	0.5596	768	0.208195993	e-bombardment
3254	1600	2640.264026	0.606	703	0.206377045	e-bombardment
3255	1600	3139.717425	0.5096	612	0.151082541	10 Min 250K
3256	1600	2982.84862	0.5364	663	0.172280347	10 Min 250K
3257	1600	2879.769618	0.5556	711	0.19136622	10 Min 250K
3258	1600	2878.215506	0.5559	673	0.181236296	10 Min 250K
3259	225	364.5495787	0.6172	101	0.214742594	10 Min 250K
3262	1600	2816.405562	0.5681	702	0.193194759	10 Min 250K
3264	225	352.0025031	0.6392	102	0.224599012	10 Min 250K
3272	1600	2896.976281	0.5523	812	0.217252365	e-bombardment
3273	1600	2866.869737	0.5581	815	0.220344935	e-bombardment
3275	1600	2846.4686	0.5621	806	0.219473489	e-bombardment
3276	1600	2851.541615	0.5611	805	0.218811221	e-bombardment
3277	1600	2813.434148	0.5687	794	0.218744514	e-bombardment
3278	1600	2860.718756	0.5593	823	0.222986255	e-bombardment
3279	1600	2853.575887	0.5607	807	0.219198476	e-bombardment
3280	225	359.6547315	0.6256	108	0.232750917	e-bombardment
3281	1600	3190.428714	0.5015	0	0	10 Min 500K
3282	1600	3190.428714	0.5015	2	0.000485886	10 Min 500K

Table A 6: Raw data for the thermal stability of surface oxygen vacancies presented in Figure 5.14 in the main text.

7.2 Oxygen Vacancy Decay on the Anatase (101) surface

The following mathematical model for the decay of surface oxygen vacancies on the TiO_2 anatase (101) surface was proposed by *Michael Schmid* [private communication]. It allows to determine the distribution of activation energy barriers for the given experimental data. Let us first assume one species with a single activation energy:

$$\frac{dN}{dt} = -NR \tag{A 1}$$

where

$$R = \nu_0 e^{-E_a/kT} \tag{A 2}$$

$$N(t)/N_0 = e^{-Rt} \tag{A 3}$$

with

N(t)	•••	Number of surface oxygen vacancies at time t
N_0		Initial number of surface oxygen vacancies
T		Temperature
$ u_0$		Attempt frequency
E_a		Activation energy barrier
t		Time

Let us now consider a distribution of species with different activation energies, $\rho(E_a)$, with

$$\int \rho(E_a)d(E_a) = 1 \tag{A 4}$$

Thus, we get

$$N(t,T)/N_0 = \int \rho(E_a) e^{-R(E_a,T)t} dE_a$$
 (A 5)

We want to solve this for $\rho(E_a)$ under condition (A 4). It is an integral equation of the form

$$g(T) = \int \rho(E_a) K(E_a, T) dE_a$$
 (A 6)

with the experimental data

$$g(T) = N(t,T)/N_0 \tag{A 7}$$

and the kernel

$$K(E_a, T) = e^{-R(E_a, T)t} = \exp(-\nu_0 t \exp(E_a/kT))$$
(A 8)

This type is known as Fredholm integral equation of the first kind [107, 108]. With a kernel of the form $K(E_a - T)$, in principle, such equations can be solved via the Fourier transform. In principle, we can achieve this by a substitution

$$x = \ln(kT) \tag{A 9}$$

$$y = \ln(E_a) \tag{A 10}$$

leading us to a kernel

$$K(x,y) = \exp(-\nu_0 t \, \exp(-\exp(\ln(E_a/kT))))$$
 (A 11)

$$= \exp(-\nu_0 t \, \exp(-\exp(\ln(E_a) - \ln(kT)))) \tag{A 12}$$

$$= \exp(-\nu_0 t \, \exp(-\exp(y - x))) \tag{A 13}$$

We can't do this via a Fourier transform, however, because the kernel function is similar to a smeared-out step function, so its Fourier transform does not converge (it is not finite). Assuming $\nu_0 t = 10^{15}$, for "reasonable" values, we must have

$$\exp(-\exp(y-x)) \approx 10^{-15}$$
 (A 14)

$$-\exp(y-x) \approx \ln 10^{-15} \approx -34.54$$
 (A 15)

$$y - x \approx 3.54 \tag{A 16}$$

So, this is roughly where the kernel function has its step. Therefore equation (A 6) was solved numerically, using a trial function dependent on a small number of parameters, and minimizing the mean square deviation of the calculated and experimental values. The trial function used in Figure 5.19 was of the form

$$C \times \left(\left(\frac{1}{2} + \frac{1}{2} tanh\left(\frac{E_a - a_1}{a_2}\right) \right) \left(\left(\frac{1}{2} - \frac{1}{2} tanh\left(\frac{E_a - a_3}{a_4}\right) \right) \right)$$
(A 17)

where C is a constant for normalization according to equation (A 4), and $a_1 \cdots a_4$ are the parameters that have been optimized.
Laser Calibration and raw data

Figure A 1 shows the intensity profile of the laser spot. Obviously the intensity distribution is not homogeneously distributed. Also there are off-center diffraction rings visible, which stem from dirt particles. Nevertheless, it was possible to adjust the beam in a way that the most homogeneous part of it would hit the sample.



Figure A 1: Intensity distribution over the area of the laser spot

To really calibrate the energy of the laser beam on the sample two experiments had to be done. In the first, the energy of the beam was measured by two power meters at different positions in the laser beam after the same number of lenses, to calibrate the two tools with respect to each other (see table A 7). The measured powers are different, because the pulse energy meter shows the intensity of every single laser pulse, while the power meter is measuring the heat, which the laser pulse produces.

Pulse energy meter I	Power meter (using an aperture
$({ m mJ}~/~{ m Pulse})$	of the same area as the sample) (W)
6	0.31
7	0.35
8	0.48
9	0.49
10	0.57

Table A 7: Calibration of the pulse energy meter to the power meter



Figure A 2: Calibration curve of the two Power meters for calibration of the laser energy

In the graph in Figure A 2 the linear relation between the two instruments is well pronounced.

In the second experiment, the power meter was inserted into the preparation chamber at the same position, where usually the sample would be. Additionally an aperture with an area of one square centimeter was mounted before the powermeter to measure the power, which would normally reach the sample. Then the values of the two instruments were recorded again and the values are printed in table A 8.

Power meter I	Power meter II (using an aperture	
(mJ / Pulse)	of the same area as the sample)(W)	
1	0.068	
2	0.145	
3	0.225	

Table A 8: Determination of the laser energy at the sample inside the chamber compared to the value of power meter I.

After power calibration the following raw data for oxygen desorption from the oxygen exposed TiO_2 rutile (110) surface was recorded.

Laser power (mJ/pulse)	Laser power (W/cm^2)	Fraction of remaining adatoms
15	8.07	0.452
20.6	10.81	0.118
25.1	13.50	0.109
31	16.68	0.098

Table A 9: Fraction of remaining oxygen adatoms after laser irradiation with different pulse energies presented in Figure 4.15 in the main text.

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