

ABSTRACT

LEED and STM Studies of Rutile (1x1) and (1x2) TiO₂(110)

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The structures and properties of rutile (1x1) and (1x2) TiO₂(110) surfaces are studied using low energy electron diffraction (LEED) and scanning tunneling microscopy (STM). For (1x1) TiO₂, LEED analysis shows common relaxation features reported in literatures: The bond length for bridging oxygen is contracted to 1.852 Å and 5-fold coordinated titanium is sagged downward by 0.182 Å. In addition, the sequence of alternatively contracted-elongated Ti-O bonds has been observed and discussed. The partial reduced (1x1) surface exposed under formaldehyde (CH₂O) environment is also investigated using variable temperature (75-300 K) STM. At low temperature, a diolate formed via coupling between two CH₂O molecules is discovered. At room temperature, such diolate is further found forming a stable coverage of adsorption.

For (1x2) reconstructed TiO₂(110), LEED simulation of Ti₂O added row model is performed with low temperature (T = 190K) experimental spectra of fractional diffraction spots. The resultant structure yields a R_p value of 0.51 which suggests an indefinite

structural correlation to the experimental data. The modeling details are discussed to explain such LEED result and suggestions are given to improve it. A novel method using a chemical probe to investigate (1x2) $\text{TiO}_2(110)$ is also utilized. TMAA as a chemical probe is dosed on the surface and imaged using room temperature STM. The adsorptions of TMAA are observed on sites of (1x2) trough and strand, and also on cross-linked sites with varying preferences. Three proposed (1x2) added row models, Ti_2O , Ti_2O_3 and Ti_3O_6 , are compared to the observed adsorption behaviors. Ti_2O added row model is found consistent with such adsorption behaviors and models of TMAA adsorptions are proposed.

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A Dissertation

Approved by Department of Physics

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Submitted to the Graduate Faculty of
Baylor University in Partial Fulfillment of the
Requirements for the Degree
of
Doctor of Philosophy

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May 2016

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ACKNOWLEDGMENTS

The author wishes to express his deep appreciation to the people who have supported him over the past years. This endeavor would not have been possible without them.

To physics department, thanks for providing a comfortable research environment for all the graduate students and professors.

To Dr. Park, thanks for your wise and patient advisement. The knowledge I learned from you will not only benefit my future career, but also guild my entire life.

To the faculties and friends who helped me in the dissertation writing, Dr. Benesh, Dr. Wang, Dr. Wu, Yang Jingyi, Ding Zhiyun, Zhu Tao, Ding Chiqun, Li Baofei, Liu Yang and Xia Yaobiao, thank you for sharing the valuable writing skills with me.

To all the colleagues and advisors in my lab, also to Dr. Russell and Dr. Ariyasinghe who gave helpful advices about my research, thanks for your professional insights and cooperation which make me a proper scientist.

Finally to my parents and wife, Huihan, your love and support are the most precious treasure.

For my passed away maternal grandfather and paternal grandmother
and for my family

CHAPTER ONE

Introduction

1.1 Applications and Research Motivation for Studying Titanium Dioxide (TiO₂)

Titanium dioxide (TiO₂) has various applications that cover many aspects of daily life and industry. For its high refractive index, white apparent color, and the safety to human and environment, it is used to produce cosmetics, pigment, paint, and optical coating. In addition, TiO₂ has important catalytic applications in industry. As a catalytic support, gold nanoparticles are dispersed on TiO₂ surface to oxidize carbon monoxide [1], and Au/TiO₂ is well known to lower energy barrier dramatically in CO oxidation [1-3]. Its application can be also found in photocatalysis [2,4], where TiO₂ plays a critical role to utilize the photon energy. For example, Honda and Fujishima effect [5] discovered that water can be decomposed into hydrogen by the electron excited by UV light in TiO₂. Later, this effect had been utilized as TiO₂ self-cleaning film. On such TiO₂ thin film, organic molecules of contaminant can be broken down first by UV light adsorption [4]. Then, the superhydrophilicity of the thin film allows a water layer to form and wash the contaminant off.

With promising outlook on these applications, the production scale of TiO₂ is already over million tons [2]. TiO₂ is usually produced and used in form of powder to maximize the surface area. A larger surface area is desired in industrial applications since

the reaction rate is proportional to the number of activation sites on surface. Because TiO_2 in the powder form contains different polymorphs, its properties including catalytic behaviors could be complex and convoluted. Discerning key and salient features in reaction mechanisms can be very difficult at times, if not impossible. On the other hand, performing experiments on a well-defined surface can provide an opportunity to understand fundamental steps in catalytic reactions. Using the knowledge gained in the single crystal study can help us to design advanced catalyst.

Various polymorphs of TiO_2 phases are known to exist. Among them, anatase, brookite and rutile are three major ones. Rutile is thermodynamically the most stable phase, and the others can be converted to rutile by heating around 1000 K. Due to its high thermodynamical stability and commercial availability in high purity form, rutile is regarded as a prototype model system to understand other transition metal oxide surfaces.

1.2 Structure of Rutile TiO_2 and (110) Surface

In a simple ionic model, two 4s and two 3d electrons of Ti atom fill 2p orbital of two O atoms, forming Ti^{4+} cations and O^{2-} anions. The rutile structure is then considered as each Ti^{4+} cation surrounded by six O^{2-} anions nearby, and each O^{2-} anion is surrounded by three Ti^{4+} cations. The repeating unit cell is a tetragonal, and the lattice constants are $a = b = 4.58 \text{ \AA}$ and $c = 2.95 \text{ \AA}$ (Fig. 1.1).

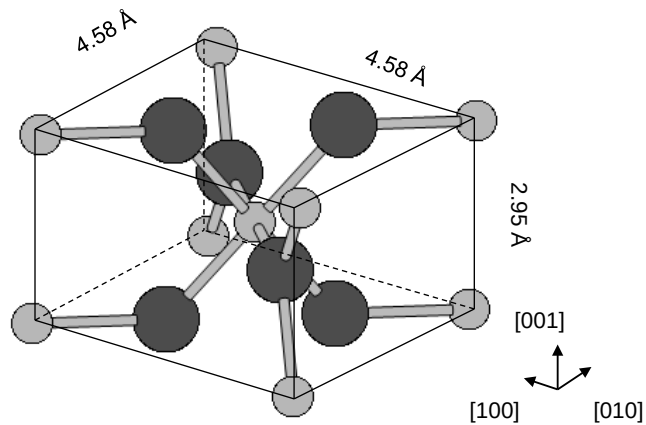


Figure 1.1 Rutile TiO_2 unit cell (Big sphere - Oxygen; Small sphere - Titanium)

More intuitively, rutile TiO_2 can be viewed as the stacked TiO_6 octahedra in edge-edge and edge-corner sharing geometry. The centered Ti^{4+} binds with four co-planar O^{2-} ions at a distance of $1.946 \text{ \AA}$ and with two apex O^{2-} ions, whose bond distances are

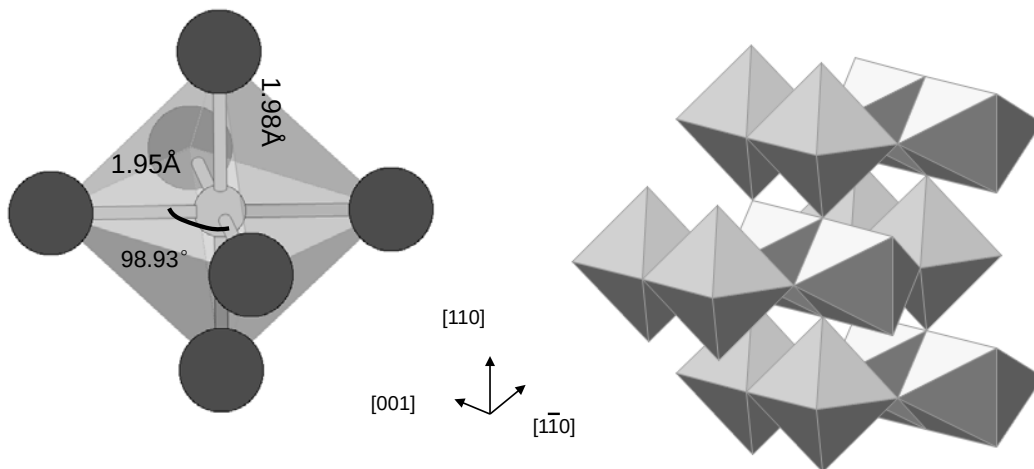


Figure 1.2 TiO_6 octahedron and edges sharing/ edge-vertex sharing configuration

$1.983 \text{ \AA}$ in the octahedron. The angle between co-planar Ti-O bonds is 98.93° (Fig. 1.2 Left). Along $[001]$, every octahedron shares the edges with adjacent ones to form

octahedra columns (Fig. 1.2, Right). A column is connected with each other by sharing its co-planar O ions with the apex O ions of the neighboring columns, which are rotated by 90° along $\langle 001 \rangle$ axis. Such an interconnected structure keeps high valance Ti^{4+} cations apart, minimizing their repulsive coulomb force [6].

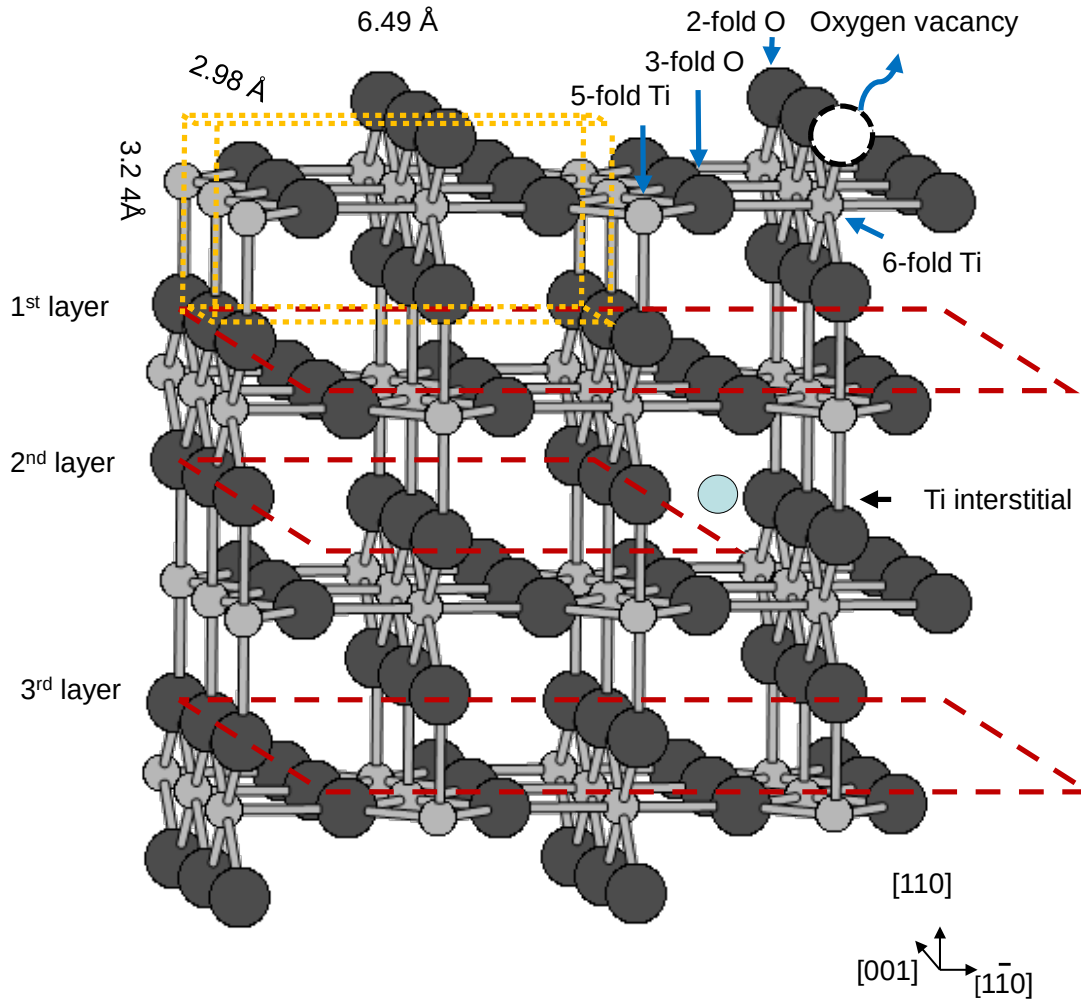


Figure 1.3 Rutile (1x1) $\text{TiO}_2(110)$ surface termination, bulk and defects (Yellow frame of dotted line – Unit cell; Red dashed line: Slab determination; Open dashed circle – Oxygen vacancy; Blue sphere: Ti interstitial)

Among many low Miller-index surfaces such as (110), (001), (100) and (011) which have been studied and reported [2, 7, 8], (110) surface has been investigated most extensively due to its lowest surface energy [9]. The basic surface termination can be understood using the rule of autocompensation [2]. It requires the same number of Ti-O and O-Ti bonds to be broken when cleaved from bulk. The dangling bonds on the Ti cations transfer electrons to O anions for the compensation of the missing charge. On (110), the longer and weaker 1.983 Å bonds are broken, and all the layers have zero dipole momentum along [110]. The surface unit cell of (1x1) TiO₂(110) has dimension of 6.49 Å x 2.98 Å x 3.24 Å, which is shown as yellow dotted line in Fig. 1.3. The unit cell is repeated in the layer below with half of the lattice constant shifted, 3.25 Å along [110]. Also the interlayer distance, *e. g.* the first and second layer, *etc.* is 3.2 Å, often referred as the step height in experiment or the thickness of a slab in theoretical calculation.

1.3 Relaxation of TiO₂(110)

In bulk where atoms are surrounded in all three dimensions, the inter-atomic force is well balanced between the attraction caused by the bonding and the electrostatic repulsion among the ion cores of the same charge. Once surface is formed, the severed bonds along outward surface normal don't provide attraction anymore and cause unfilled orbitals on the surface. As consequence, surface atoms are displaced from their bulk positions to compensate both the absent bonds and unfilled orbitals. The surface

relaxation of (1x1) $\text{TiO}_2(110)$ has been investigated using density function theory (DFT), Low Energy Electron Diffraction (LEED) and Small Angle X-Ray Diffraction (SAXRD) [10-12]. From these studies, a number of commonly observed features emerge. Generally, the bridging bond between 2-fold oxygen and 6-fold titanium contracts (see Fig. 1.3); The 5-fold titanium on surface is sagged inwards to the bulk; The bond between the 6-fold titanium in the first layer and the oxygen, which is underneath this titanium and positioned on the edge of octahedra, is elongated. In this dissertation, the surface relaxation is revisited using LEED analysis, and a detailed calculation is presented in CHAPTER FOUR.

1.4 Defects on $\text{TiO}_2(110)$

Various defects can form on $\text{TiO}_2(110)$ from point defects such as oxygen vacancy and titanium interstitial to extended defects, for example, step edge. The step edge is formed as a terrace-step structure when annealing restores the ion sputtering-damaged (110) surface. The terrace height is 3.2 Å, one lattice constant along $[\bar{1}10]$, as a result of partially removing one unit cell layer. The step boundaries typically run along $\langle 001 \rangle$ and $\langle \bar{1}11 \rangle$. The point defects such as bridging oxygen vacancy and titanium interstitial can be viewed as non-stoichiometric defects. On the surface, the bridging oxygen vacancy is formed by missing of 2-fold oxygen (Fig. 1.3, dashed circle). As a result, it exposes titanium ions underneath and reduces their oxidation state to Ti^{3+} . These point defects are

commonly present in experiments and their surface coverage can reach as high as 10% depending to the reduction level. And, many believe that point defect plays an important role in the surface chemistry of $\text{TiO}_2(110)$. Likewise, excessive titanium resulting from loss of oxygen (Fig. 1.3, blue sphere) may diffuse interstitially into bulk. These bulk defects are believed to cause the change of electrical and optical properties of TiO_2 , which make its applications of photocatalysis and photo-voltage possible [1, 4].

1.5 Extend Defects on $\text{TiO}_2(110)$

In a typical experimental preparation, TiO_2 can go through a reduction process via de-oxygenation and may gradually transform into TiO_{2-x} ($x < 0.0035$) [2]. As reduction level increases, the concentration of titanium interstitial can increase in bulk. Because the titanium interstitial is coordinated at the center of oxygen octahedral channel, it changes the edge-edge and corner-edge sharing structure in rutile TiO_2 to face-face sharing. In bulk, such transformation can result in crystalline shear plane (CSP) as illustrated in Fig. 1.4. Two octahedral structures (Blue and Orange) are joined along $[1\bar{1}0]$. The adjacent octahedra can deform and further share one of their faces with each other. By sharing the faces in such way, the height difference between two Ti ions at the center of octahedra becomes half the lattice constant – 1.6 Å. In this configuration, the local coordination and geometry around the titanium ions are still structurally identical to those in parent structure. CSP or face sharing octahedral are hallmark in many sub-oxides of

TiO₂, well known as Magnelli phases from corundum, monoxide and eventually to metal. Their stoichiometry can be reduced as Ti_{2n}O_{2n-1} ($n \geq 1$ integer) as n decreases, and the structures of these sub-oxides are markedly different.

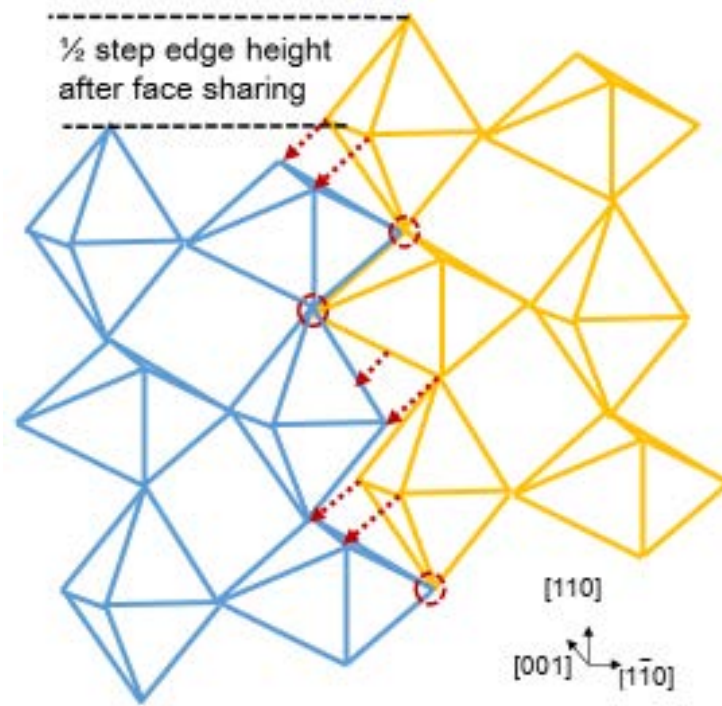


Figure 1.4 Crystal shear plane between two rutile TiO₂ terraces (Red dashed line and circle, vertex of sharing faces)

The reduction process is also believed to cause surface phase transition from (1x1) to (1x2) reconstruction on rutile TiO₂(110) although the exact nature and structure of (1x2) is still intensely debated. The (1x2) TiO₂ surface is commonly characterized as row-like structures added on (1x1) TiO₂(110) [13]. In STM image (Fig.1.5a), the row-like structure extends from step edge along [001] with apparent width of 13 Å - the doubled periodicity in [110]. The apparent height of the reconstructed row is 1.6 Å.

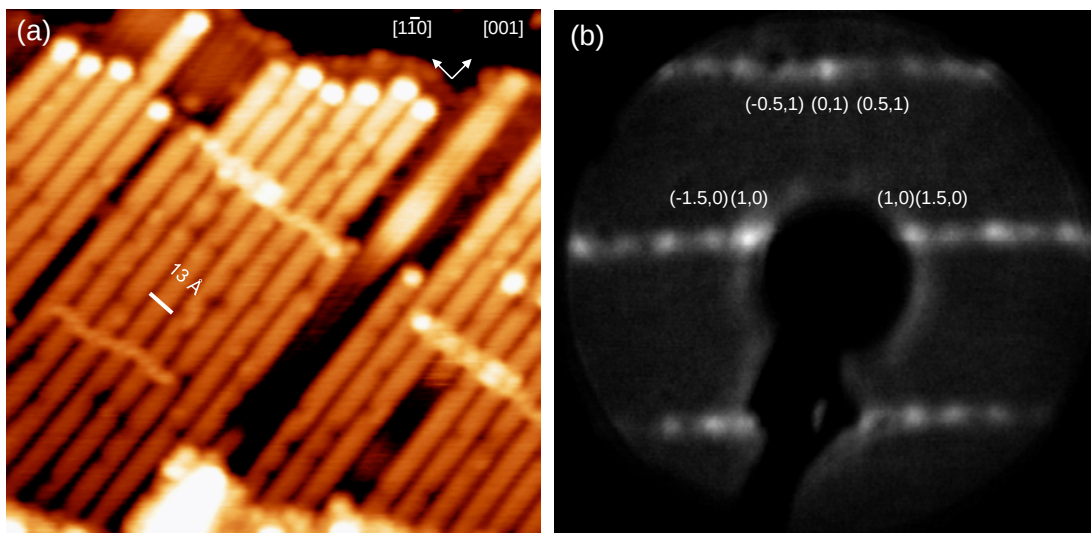


Figure 1.5 (a) STM image and (b) LEED diffraction spots of (1x2) TiO₂(110)

In LEED pattern (Fig. 1.5b), the reconstruction results in fractional spots between integer spots.

Different models have been proposed to explain the (1x2) structure [13, 14]. Most of the models can be viewed as various add-on structures (Fig. 1.6, yellow dashed box and circle) over two adjacent (1x1) surface unit cells. The repeating add-on structure along [001] can therefore represent the extended rows observed in STM image. Among these models, the Ti₂O₃ added row modeled by Onishi and Iwasa [14] has long been used to explain the stoichiometry and structure on (1x2) TiO₂(110). Its add-on structure has two Ti and three O atoms (Fig. 1.6a). One O atom is sitting above the centered Ti cation of two adjacent (1x1) surface unit cells. Two Ti cations are aligned to this added O anion along [110] as well as to two bridging O anions of the underlying surface unit cells.

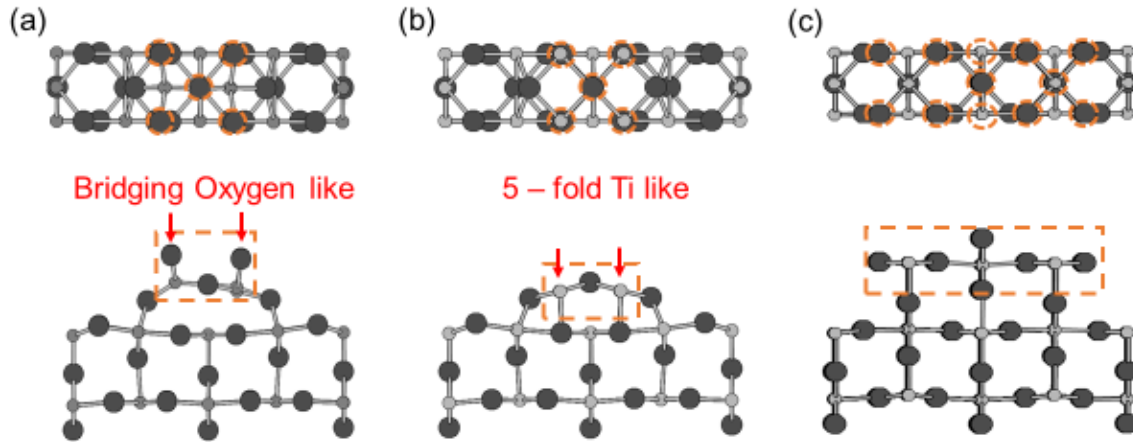


Figure 1.6 Top view and side view of models for (1x2) reconstruction: (a) Ti₂O₃ added row; (b) Ti₂O added row; (c) Ti₃O₆ missing row (Darker sphere: O Lighter sphere; Ti)

The two Ti cations are bridge-connected to those in the next unit all along [001] via two additional O anions. Although the stoichiometry of this added row is like that of corundum phase (Ti₂O₃), the structure is not actually related to it as the Ti cations occupies the sites corresponding to the interstitial sites of the rutile lattice.

Later, Park *et al.* [13] proposed an alternative model which is similar to corundum structure: Ti₂O added row (Fig. 1.6b). In this model, the same additional O anion of the Ti₂O₃ model is sitting above the centered Ti of the (1x1) surface unit cells. Unlike the Ti₂O₃ model, there is no additional bridging O atoms. And, the two Ti cations are displaced for a half lattice constant along [001]. They are centered in a roughly square plane formed by bridging O atoms and additionally centered O atom. And, they sit above the 3-fold oxygen on the (1x1) surface unit cells. The two half-octahedra formed by these two Ti atoms and their surrounding O atoms forms face-sharing with the octahedra on the

(1x1) surface unit cell. Such sharing can be viewed as TiO_2 octahedra being slipped and stacked on surface as a similar structure of corundum.

In contrast to the two models describing (1x2) reconstruction as oxygen-deficient, sub-stoichiometric structure, Bowker and Bennett [15] proposed a row model made of Ti_3O_6 units for the so-called cross-linked (1x2) reconstructed surface (Fig. 1.6c). Its add-on structure has three stoichiometric TiO_2 units built on top of (1x1) surface unit cell and at their bulk positions. Consequently, this model can be viewed as a bulk-terminated, corrugated and stoichiometric surface. The stoichiometric nature of this model despite such a fact that the cross-linked (1x2) reconstruction requires higher preparation temperature. The Ti_3O_6 model had not received much attention until Pieper *et al.* [16] used it to support their non-contact atomic force microscopy study.

The proposed models of Ti_2O_3 and Ti_2O have been investigated by other researchers, and their conclusions are still debated [17-19]. M. Blanco *et al.* examined both models by best-fitting their theoretically optimized structure to experimental LEED data. It was suggested that the structure of Ti_2O_3 added row can generate more favorable correlation to their experiment data rather than Ti_2O added row. On the other hand, High Resolution Transmission Electron Microscopy (HRTEM) study by Shibata *et al.* shows that additional Ti cations on (1x2) reconstruction are coordinated with surface O anions as in the Ti_2O added row model rather than in the Ti_2O_3 model. Because of these

contradictory findings, a dynamic LEED simulation and LT experiment have been performed to investigate Ti_2O added row in CHAPTER FOUR.

1.6 Chemistry on Reduced $\text{TiO}_2(110)$ Surface

Defective sites on reduced $\text{TiO}_2(110)$ (*e.g.* bridging oxygen vacancy) is proven reactive towards many organic/ inorganic molecules in atmosphere (*e. g.* H_2O , O_2 , CO and carbohydrates) [2, 3, 20, 21]. These catalytic reactions occur as either physisorptions or chemisorption on surface at first. The molecules can sequentially diffuse to defect sites lowering their energy. These adsorbates can further lower energy as they are partially dissociated at the defects or activated, and consequently participate in chemical reactions [22-27].

Formaldehyde is a common indoor pollutant existing in commercial building materials. It is also a product of bio-mass processing, which uses bio-resources to produce alternative energy [23, 25, 26]. The reactivity of reduced $\text{TiO}_2(110)$ toward formaldehyde is potentially important as pollutant removal or novel energy production. Recently, a TPD study [25] reported that, formaldehyde adsorbed on reduced $\text{TiO}_2(110)$ and then C_2H_4 can be produced as thermal desorption. It suggested the formation of C_2H_4 is made possibly via carbon-carbon coupling between two formaldehyde adsorbates. Since carbon-carbon coupling is an essential step to polymerize large organic molecule as industrial products [25, 28], its fundamental mechanism may be a key to a future catalytic

engineering. In CHAPTER FOUR, chemical coupling of formaldehyde on reduced $\text{TiO}_2(110)$ is investigated using *in situ* STM.

1.7 Chemical Probe on Defective $\text{TiO}_2(110)$

Many organic molecules contain various functional groups whose reactions are unique toward specific sites on a metal oxide surface are well characterized. In principle, they can be employed as a reactive probe molecule to map the structure of the clean surface and allow researchers to extract its site-specific atomic information. Onishi and Iwasawa performed a STM study of formate ions dosed on (1×1) $\text{TiO}_2(110)$ [29]. They found formate ions adsorbed on the sites of protruded lines appearing in its image of empty state STM. The adsorption preference of formate ion on 5-fold Ti^{4+} sites of $\text{TiO}_2(110)$ was also predicted by DFT calculation. Thus, it is confirmed that the 5-fold Ti^{4+} chains appear as protruded lines as electronic effects, in contrast to the other belief that such lines stand for the 2-fold O^{2-} cations, which occupy higher positions along [110].

The contentious (1×2) structure can be also investigated similarly using a probe molecule with STM. The previously introduced, Ti_2O_3 , Ti_2O , and Ti_2O_6 added row models have significant differences in geometry and composition. The Ti_2O_3 row is terminated with bridging O like added anions, whereas the Ti_2O model has 5-fold Ti like ions exposed on the row surface (Figure 1.6, Left & Middel). All of their additional Ti

cations are apart in a distance of roughly a half lattice constant along $[1\bar{1}0]$. However, the Ti_3O_6 model has the (1x1)-like surface for the row and its surface 5-fold Ti ions are one lattice constant apart. Trimethyl acetic acid (TMAA), whose interaction on (1x1) surface has been well understood [30, 31], can be used as suitable chemical probe to identify the 5-fold Ti like sites. The detailed investigation of TMAA chemical probe to (1x2) surface is reported in CHAPTER FOUR.

CHAPTER TWO

Experiment

2.1 UHV Requirement and Maintenance for Surface Study

Maintaining cleanliness and controlling contamination on a specimen surface are essential in studying surface structure, defects and reactivity. To achieve these goals, a vacuum system is used. A vacuum environment of low background pressure can limit contamination rate and provide researchers sufficient time to conduct experiment. Achieving ultra-high vacuum (UHV) with a base pressure lower than 10^{-10} Torr, is a routine pre-requisite for many experiments [32].

In order to maintain an UHV chamber with 10^{-10} Torr or a lower pressure, sources of contaminants should be strictly avoided or limited. Usually, residual gases are the major contaminants due to molecular adsorptions on specimen surface. At 10^{-10} Torr, the majority of residual gases is H_2 . The collision rate between gas molecules and the specimen surface is as low as $4 \times 10^{-10} \text{ cm}^{-2} \text{ s}^{-1}$ [33]. It reduces the possibility of surface reactions and therefore keeps the surface cleanliness. Therefore, UHV provides hours of experiment time before a significant portion of surface may be contaminated.

2.2 Vacuum Pumps in UHV System

2.2.1 Rotary Vane Pump/ Roughing Pump

In order to achieve and maintain UHV condition in a chamber, a number of different pumps are utilized over the wide pressure range from the atmosphere pressure to UHV regime (Fig. 2.1). A differential pumping system which combines a rotary-vane pump and a molecular turbo/ drag pump, an ion pump and a titanium sublimation pump (TSP) are commonly used to reach UHV.

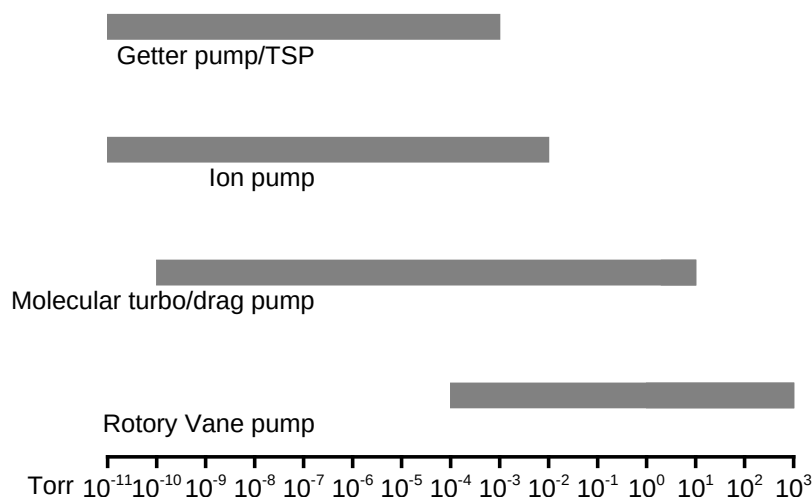


Figure 2.1 Pump operation pressure range

Rotary-vane pump serves as a fore/ roughing pump on the high pressure side of a differential pump to provide a necessary fore-line pressure of 10^{-2} Torr for a molecular turbo/ drag pump. It has an off-center rotor with two spring loaded vanes in a cylinder stator with an inlet and an oil sealed outlet (Fig. 2.2). Spring loaded vanes rotate with the rotor tangential to the cylinder wall. The cylinder stator is divided into three volume-variable spaces by rotating vanes, and two of them circularly admit gas from inlet

or squeeze gas into outlet. The oil in reservoir forms thin film on the stator, rotor and vanes, and it serves as both sealant and lubricant in operation. Because the use of oil generates micrometer-size droplets [33], an oil insulating valve should be placed in the fore-line and properly operated in pump start-up/ shut-down to prevent a possible backflow toward the UHV area. A rotary vane pump of dual-stage configuration can reach the ultimate pressure down to 10^{-4} Torr with an improved pumping efficiency.

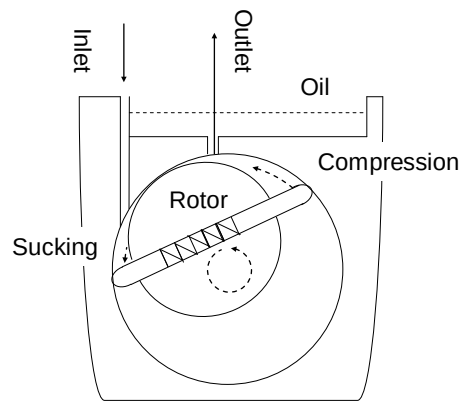


Figure 2.2 Rotary vane pump

2.2.2 Molecular Turbo/ Drag Pump (TMP)

Molecular Turbo/ Drag Pump (TMP) operates on the low pressure side of differential pumping. It consists of a high vacuum stage of turbo molecular pump and a low vacuum stage of molecular drag pump. Two stages are built coaxially in the pump body. The molecular drag stage improves the pressure tolerance in the fore-line up to 10 Torr range. Thus, it provides an additional protection of the fragile components of the turbo stage when operational mishap possibly occurs in a high fore-line pressure.

The molecular turbo stage consists of the interleaved rotor and the stator blades (Fig. 2.3A). The rotors spin at a high rotational speed from 1000 Hz to 1500 Hz depending on the size of turbo pumps. The gas molecules collide with the series of high speed rotor blades set up at different angle and lose their momentum along the exhaust. Next, they collide with stator blades and make the further deceleration for compression. Rotor-stator compressors are arranged stage by stage to achieve an exponential increase in the compression ratio. The compression ratio varies in different molecules. It is approximately proportional to the square root of molecular weight [5].

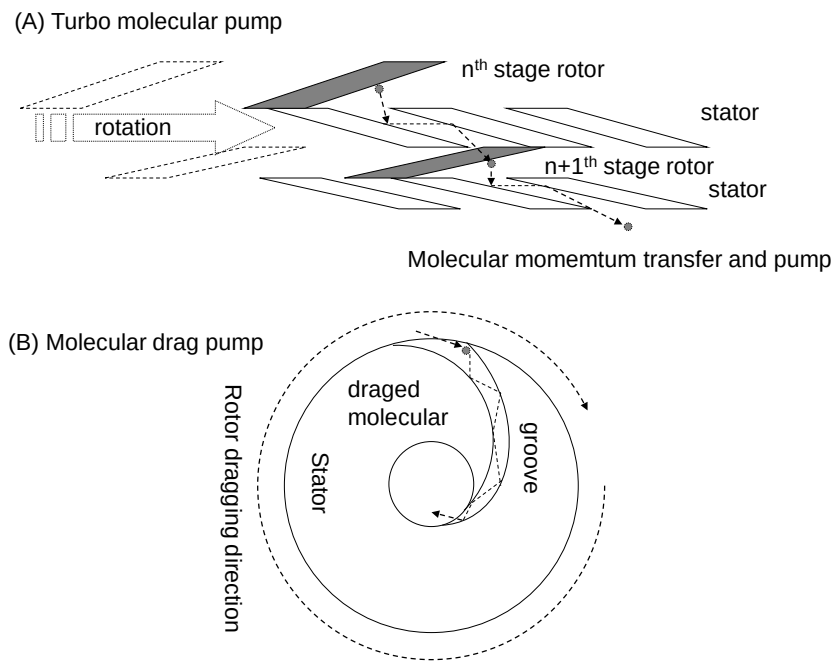


Figure 2.3 Molecular turbo/ drag pump

In the molecular drag stage (Fig. 2.3B), molecules are dragged and accelerated tangentially by the high speed spinning rotors. The compression is achieved by helical

guiding grooves, which are engraved toward exhaust on a stator. When molecules are dragged into the groove by rotor and collide with the wall of grooves, they are radially decelerated and compressed. Finally, they are dragged and pumped to the outlet near the center of stator surface.

2.2.3 Titanium Sublimation Pump (TSP)

Titanium sublimation pump serves as an auxiliary pump in UHV system. Unlike the other pumps, it is designed to operate intermittently. The working principle of TSP can be understood using Fig. 2.4. It sublimates reactive metal on a high temperature alloy filament (usually titanium-coated tungsten). The evaporated metallic vapor is then deposited on the pump shroud. The residual gas in the chamber reacts with its

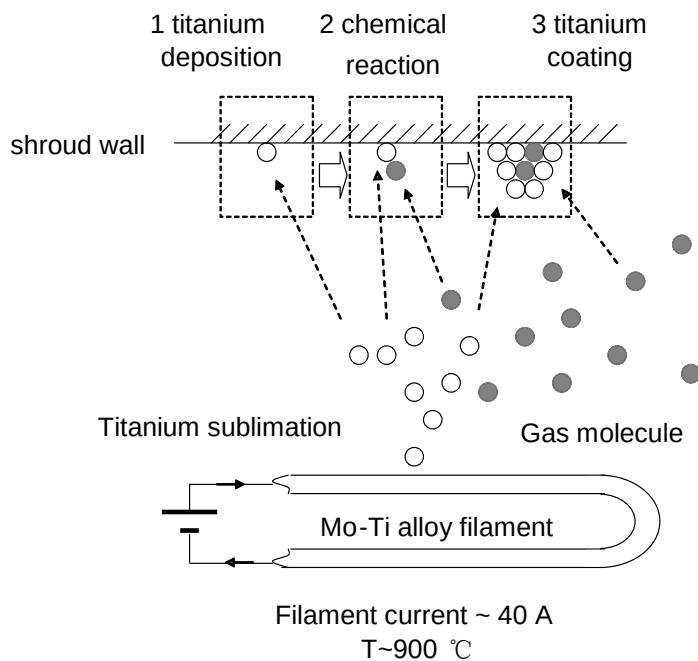


Figure 2.4 TSP and getter pumping mechanism

deposited layer on the shroud wall and forms a non-volatile reaction compound. Hence, it is also called getter pump [33].

In a typical TSP operation, the pressure will increase slowly after it is turned on. In the beginning (Fig. 2.5, phase I), a high current (~ 40 A) is flowing through the filament and gradually heating it up to a temperature over 900°C (Fig. 2.4). Gas molecules are desorbed from the filament and the surface of shroud wall to cause the pressure increase.

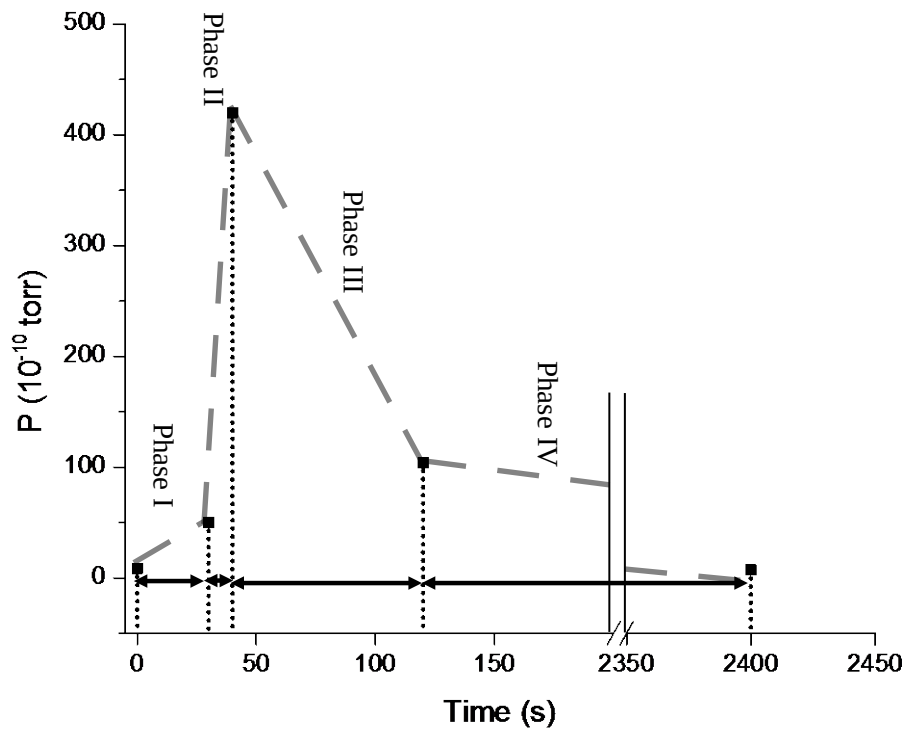


Figure 2.5 TSP pumping curve and TSP cycle

In the phase II, two effects acting on the pressure are competing against each other. On one hand, the pressure increases because of titanium sublimation. On the other hand the pressure decreases due to the getter pumping effect. Initially, titanium sublimation

accelerates and contributes to the rapid onset of pressure increase since the filament reaches the working temperature. At the same time, the area of titanium layer deposited in surrounding, which is proportional to the pumping speed, increases as well. The getter pumping starts taking place and decreasing the pressure. However at this stage, the pressure increase caused by the titanium sublimation still dominates. In the phase III, the area of deposition layer and pumping rate rapidly increase and the pressure quickly falls. The effect of getter pumping is dominating in this period.

In the beginning of phase IV, the chemically reactive gases are almost depleted, and the pumping rate decreases. Further increase in titanium deposition layer cannot improve vacuum any more. Therefore, the filament should be turned off to prevent further sublimation and unwanted deposition on the surrounding. However, the titanium deposited layer is not saturated, the consequent slowly pumping can still last until the next TSP circle needs to be started.

Because TSP results in titanium coating in the surrounding area of the filament, a care must be exercised in the positioning of TSP in an UHV chamber. Shrouding TSP in a side arm/ elbow can effectively prevent unwanted coating on other key parts of the chamber. Additionally, the use of LN₂ cooling can accelerate the surface condensation and thus increase pumping speed to a double or triple times [33]. Since the TSP pumping relies on the chemical reactions with titanium, non-reactive gases such as methane and noble gas (e.g. Ar, He) cannot be pumped except in a combination of TSP and ion pump, which will be discussed in Sec. 2.2.4.

2.2.4 Ion Pump

Ion pump is a popular choice for the main pump in a UHV system due to its higher efficiency in a pressure range of 10^{-11} Torr and a higher pumping speed of H_2 . Its non-mechanical and outlet free design makes it especially attractive for the UHV pumping need.

The range of working pressure for an ion pump is generally $10^{-2} - 10^{-11}$ Torr, and its life time varies with working pressure. A typical ion pump can continually work for 6 years at 10^{-6} Torr, but it can only work for hours at 10^{-3} Torr [32, 33]. As ion pump reaches its life time, pumping efficiency will be degraded because of pump cathode saturation. A re-activation procedure of baking over 300°C for 36 hr can restore its pumping capability. Therefore in order to prolong the life time, a turbo pump is first utilized to bring the pressure down to 10^{-6} Torr or an even lower pressure before starting ion pump.

An ion pump ionizes gas molecules in over 7000 V potential difference (Fig. 2.6). For an enhanced ionization probability, its anode is built as penning cell to trap the electron in magnetic field. The field increases the collision rate between the electrons and gas molecules. The ionized gas molecules are then accelerated and hit built-in the cathode plates, which are made of chemically reactive metal, *e. g.* titanium. Therefore, the removal of these ions is similar to the getter mechanism in TSP. Chemically reactive gases (*e.g.* H_2O ; N_2 ; CO_2) react with titanium and are chemisorbed as non-volatile

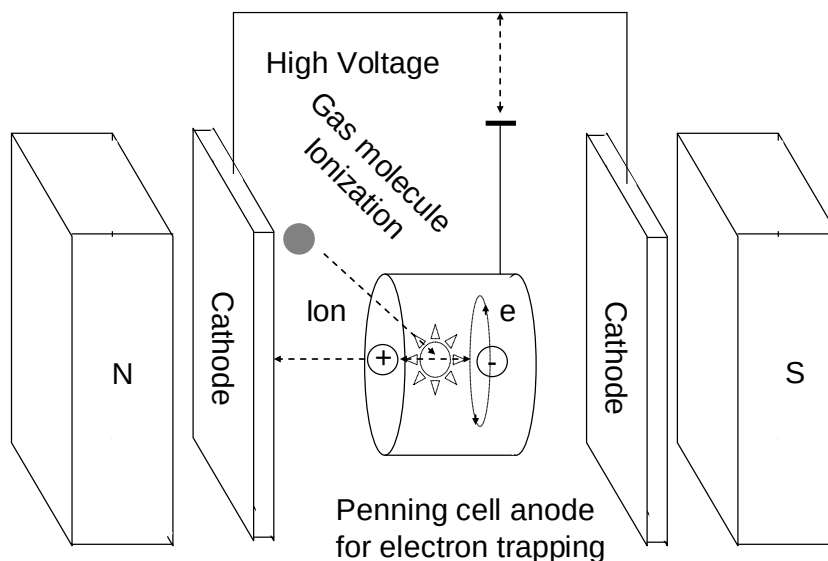


Figure 2.6 Diode ion pump

compounds. Chemically inert gases (*e.g.* Ar & He) are only buried as physisorption. When an inert gas like argon is present, the high energy Ar ions can bombard the cathode plate and sputter off or degas adsorbed gas molecules. In such case, the pumping efficiency is significantly diminished, and this is referred as argon poisoning. In order to avoid Ar poisoning, it is advised to isolate the ion pump from the chamber with a gate valve, and to pump the chamber only using the turbo pump right after using the inert gas for sputtering procedure.

Various configurations of ion pump are developed for better handling of inert gases. For example, starcell ion pump possesses outstanding pumping efficiencies for Ar and He (Table 2.1). Its pumping efficiencies for other residual gases such as H_2O , H_2 , CH_4 , N_2 , O_2 and carbon oxides are also excellent or good. In contrast, the traditional diode ion

Table 2.1 Gas pumping efficiency rating for different pumps.

Gas/ pump	H ₂	He	H ₂ O	CH ₄	N ₂	O ₂ ,CO,CO ₂	Ar
Diode	B	D	B	C	B	B	D
Starcell	C	A	C	B	C	C	A
TSP	B	N	B	N	B	A	N

A-Outstanding B-Excellent C-Good D-Poor N-None

pump which possesses better pumping efficiencies for H₂ and H₂O, the major contributions to the UHV pressure, remains as the choice for achieving the lowest ultimate pressure. For the other residual gases such as N₂, O₂, CO and CO₂, it also exhibits better performance than the starcell one. To handling non-reactive gases like He, Ar and CH₄, an integrated TSP/ diode ion pump can be used. When TSP is working, the cathode of ion pump can be regenerated by new titanium deposition. The deposition layer on the cathode therefore buries unstable implantation formed from these gases, and enhances the pumping efficiency. In this combination, TSP also provides outstanding efficiencies for pumping oxygen and carbon oxides.

2.3 A Brief Overview of Procedures in Achieving UHV

In achieving UHV, cleanliness of any parts in an UHV chamber is of utmost importance. No oil/ grease should be introduced into the UHV chamber. In order to prevent vacuum leakage, all flanges should be tightened correctly so that their knife-edges form air-tight seal with copper gaskets. After the chamber is pumped down to

pressure of 10^{-6} Torr, it should be baked typically for over 48 hours to remove water molecules in residual gases. In baking the chamber, a care should be taken to distribute heat evenly and make sure that the chamber temperature reaches about 120 °C. After baking is done, further degassing of major instrument parts (*e.g.* sample stage, ion gauge, electron gun and residual gas analyzer) is necessary to bring base pressure down to 10^{-10} Torr.

At a pressure of 10^{-10} Torr, residual gas molecules still keeps desorbing from the chamber wall. To further improve the pressure down to 10^{-11} Torr, optimizing H_2 pumping is essential. Only TSP and ion pump should be used for 10^{-11} Torr due to their highest H_2 pumping efficiencies (Tab. 2.1). The low H_2 compression of turbo pump limits its effectiveness and it should be used only for argon removal to prevent the Ar poison to ion pump.

If an even lower base pressure (*e.g.* XHV, extreme high vacuum $< 10^{-12}$ Torr) is desired due to future experiment consideration, new types of pump should be considered. For example, a high H_2 compression designed tandem turbo pump [34] may be connected in series to turbo pump. In addition, a non-evaporable getter pump (NEG) [33] can be introduced for its high H_2 pumping efficiency.

2.4 Specimen Preparation

2.4.1 Ex Situ Preparation

Specimens of high purity used in this dissertation are usually purchased from a commercial company. Generally, a surface is covered with ambient gas molecules in the air. When the specimen is introduced into a UHV chamber, it becomes the biggest source of outgassing. Depending on conditions of the surface and the types of contaminants, it can be used with a minimal treatment such as brief heating (also known as flashing). Otherwise, it must go through *ex situ*/ *in situ* treatment.

A single crystal TiO₂ surface can be easily contaminated due to its reactivity toward organic molecules or water [5, 21, 24, 35]. Such impurities cannot be removed by the common solvent flush, but by ultrasonic cleaning method. An ultrasonic cleaner generates cavitation bubbles whose pressurized wave disintegrates and disperses the contaminants into the solvent. After ultrasonic treatment, the specimen is first flushed with clean solvents to remove any residuals and then dried with pure N₂ gas. However, ultrasonic cleaning can cause electro-chemical erosion and damage some specimens. Therefore, pre-caution should be exercised.

Molybdenum disulfide and Highly Orientated Pyrolytic Graphite (MoS₂, HOPG) are often used as reference specimen in surface analysis. They both have the lamellar structures in which the bonding along [0001] is much weaker than the other orientations due to van der Waals interaction. Such a surface is chemically inert, and simple peeling can be performed *ex situ* with scotch tape. A pristine surface can be exposed by peeling

off surface layers, and it can be subsequently introduced into an UHV chamber immediately.

2.4.2 In Situ Preparation - Ion Sputtering/ Thermal Annealing

Except chemically inert surfaces such as HOPG(0001) and MoS₂(0001), the exposure to atmosphere results in a surface covered with ambient gases and unsuitable for surface studies as is. Therefore, *in situ* cleaning in UHV is typically required. Because many contaminants are chemically adsorbed on the specimen surface, its under-layers need to be exposed to restore the pristine atomic structure. Ion sputtering is utilized for this purpose to remove the contaminated surface layer.

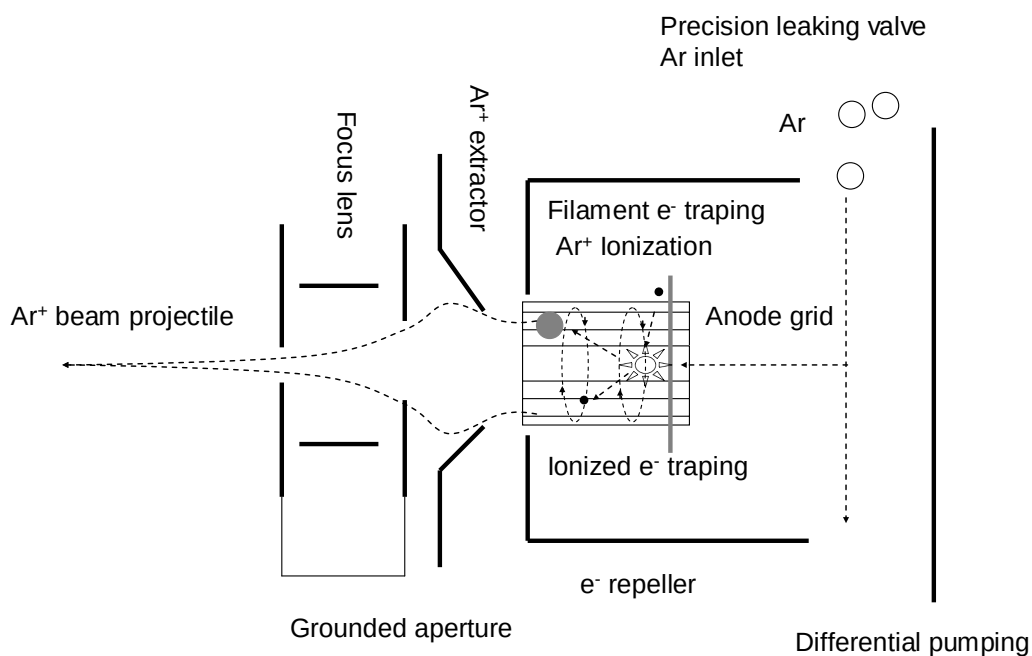


Figure 2.7 Ion gun schematics (Gray sphere - Ar⁺, Black sphere - e⁻, Black circle Ar⁺, Slash arrow - moving projectile)

Omicron ISE 10 ion gun (Fig. 2.7) is used for ion sputtering in this work. In its configuration, argon gas is filled into the ionization chamber of the ion gun (with electron repeller, anode grid and circular filament inside) and differentially pumped out of the system to avoid the pressure increase in the main UHV chamber. Electrons which are emitted from a circular filament anode (gray line), and then accelerated by a voltage applied on anode grid to ionize Ar. The electrons with the secondary electrons generated from Ar ionization are trapped in a specially designed chamber to further increase ionization probability. The ions are extracted from this chamber by the extractor and accelerated through the first grounded aperture. Ar^+ ions are subsequently condensed by a cylindrical lens and focused through the final aperture as an ion beam.

The chemical inertness and relatively heavy atomic mass of argon makes it a universal choice for effective sputtering. In a typical operation, argon gas is stored in a pressurized bottle and administered into the ion gun using a precision leak valve.

In ion sputtering, the ions with large momentum destroy and remove the impurities, contaminants and the specimen structure unselectively. The sputtering effect to a surface varies considerably with incident angles of ion beam. The ion beam in a large incident angle (measured from surface normal) creates smaller surface roughness but a bigger sputtered area. The horizontally transferred momentum from ion beam can produce secondary ionization from the surface and further function as secondary sputtering. Because of such ion cascade, large angle sputtering provides a high cleaning efficiency to expose the pristine under-layer of specimen.

A bigger sputtered area using a large angle may pose a problem as parts other than the sample surface (*e. g.* sample clips holding the specimen) may be in a line of sight and sputtered as well. Then, sputtering ion beam may dump the foreign materials onto the specimen. Alternatively, normal incident sputtering is less likely to dump foreign material onto specimen since the sputtering area is much smaller and focused. Also, considering the fact that mean free path of gas is in meters (for a sputtering pressure, 10^{-6} Torr [32]), much smaller than centimeters range for the specimen-ion gun distance, the out-going sputtered atoms from the surface have a negligible chance to bounce back and form contamination again. However, normal incident sputtering does not benefit much from the vertical ion cascade because the secondary sputtering is mainly directed toward bulk. In addition, the vertical ion cascade can implant the surface contaminants as well as Ar ions into specimen and can cause a higher surface roughness.

The Ar^+ beam from Omicron ISE 10 ion gun is calibrated for its beam size and current as a function of the beam voltage. The beam size is measured by naked eyes, estimating the size of a fluorescent spot on the reference sample with an opening of 10 mm diameter (Fig. 2.8, Left; Beam spot - central bright spot; reference center slot - solid lines). The beam spot size in the figure appears larger than the actual measurement due to the limited spatial resolution of the image by the CCD camera used in the lab. The beam current is recorded by a digital multiple meter. As shown in Fig. 2.8, the beam diameter is negatively correlated with the beam energy. On the other hand, the beam current is proportional to the voltage up to 2 kV, about which the beam current remains fairly

constant between 1.2 μA and 1.3 μA . The calibration data (Fig. 2.8, Right) also shows the ~ 7 mm spot size of Ar^+ beam with over 3.5 kV energy is small enough (< 10 mm) to avoid the ion beam dumps the foreign impurity from the sample slot edge to the specimen. Therefore, the 3.5 kV setting is on the optimal values, which can be used for sample cleaning.

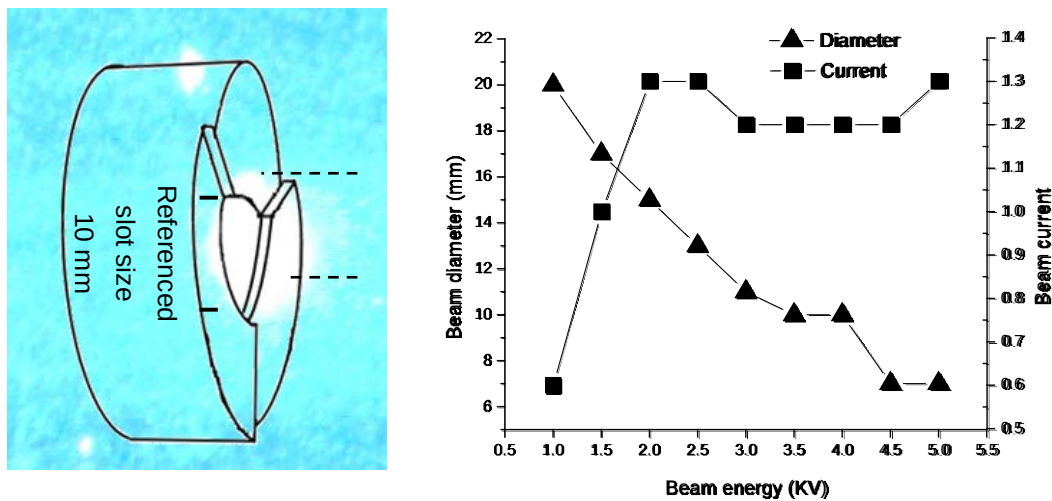


Figure 2.8 Ion gun calibration (Left: specimen holder profile mapping and image of fluorescent of 5 KV Ar ion beam spot with contrast change cause by CCD; Right: Ion beam diameter and current with the best focused setting)

An ion-sputtered surface is generally too rough and inhomogeneous to meet the requirement of surface study. Thermally assisted surface regeneration, also known as annealing, is therefore necessary. Sputtering and annealing are performed alternatively and repeatedly as typical *in situ* cleaning cycles. Direct resistance heating and high voltage e-beam heating (Fig. 2.9) are all utilized in this work. For resistive heating

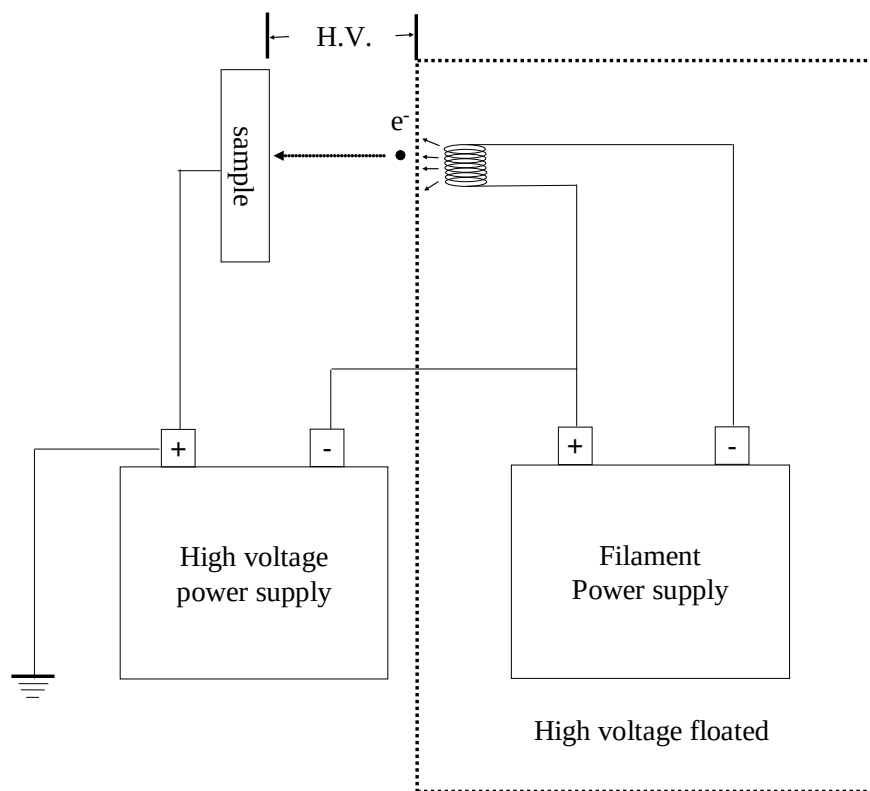


Figure 2.9 Floated e-beam heating mechanism

method, the radiation emitted by a high temperature filament directly heats the specimen. For the e-beam heating method, a power supply is used to provide a filament current. An additional high-voltage power supply provides a negative high voltage to float the filament and filament power supply. In this way, the thermal electrons from the filament surface are extracted by potential difference, and form electron beam to bombard and heat the specimen. Because the voltage can be as high as several hundred volts, it utilizes much higher power density to anneal the sample than that of resistance heating. Due to the high voltage, the filament and wiring must be protected by the electrical isolation of the circuit to avoid the potential electrical shock.

Rutile TiO₂ sample (5 mm x 10 mm x 1 mm) used in this dissertation is cleaned by cycles of Ar ion beam sputtering (1 kV; 6 μ A of sample current) for 10 minutes followed by annealing at temperature up to 900 K for 10 minutes. The sample temperature in annealing is calibrated by the direct measurement ($\Delta T \sim 5$ K) with a type K thermocouple glued on a reference surface using UHV compatible AREMCO ceramic adhesive. The sample generally undergoes several cleaning cycles until large terraces ($> 200 \text{ \AA} \times 200 \text{ \AA}$) of 1×1 periodicity are observed with little or no impurities in STM images. Repeated cycles of sputtering and annealing gradually change the sample color from pale white to blue, indicating that the sample is reduced. Therefore, a care must be exercised as it is well-known that a highly reduced sample can possess bulk defect such as CSP as well as (1×2) or other surface reconstructions.

In order to prepare a (1×2) reconstructed surface, a (1×1) TiO₂(110) sample (10 mm x 5 mm x 2 mm) sample is sputtered by 1000 eV Ar⁺ (3 μ A beam current) followed by annealing at a higher temperature, 1100 K, for a longer time period of 15 minute. The sample is subjected to repeated cycles of sputtering and annealing until a bright 1×2 diffraction pattern is observed with the LEED optics.

2.5 Surface Analysis Techniques

2.5.1 Scanning Tunneling Microscopy (STM)

Scanning tunneling microscopy measures tunneling current (I_t) between a biased tip of atomic-scale size and a conducting specimen (The tip is made of etched tungsten or

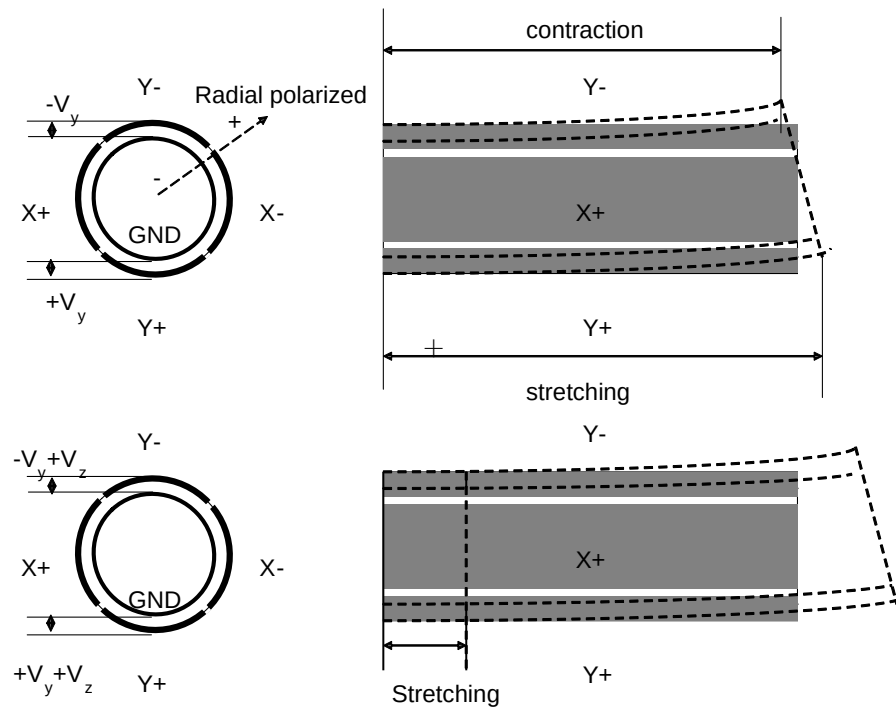


Figure 2.10 Scanning tube

cut platinum wire). It is mounted on and driven by a piezo ceramic scanning tube to raster scan over specimen surface. The scanning tube is polarized in radial direction over 1500V/ mm potential difference. The floating and the grounding electrodes are coated outside and inside the tube, respectively in symmetrical quadrants (Fig 2.10). The opposite voltages are applied for each pair of X or Y electrodes to control the raster scan and scan area along the corresponding directions. The opposite DC voltages (Fig 2.10, $V_{x/y}$ for X/ Y direction) applied on the X/ Y electrode bend scanner toward the desired direction. A global offset on these voltages is applied for the tube's stretching and contraction along Z direction. At the same time, an offset DC voltage, V_z (applied on both X/ Y signal) keeps a distance between the tip and the specimen surface. The control of

scanning size and raster grid (Fig. 2.11) is accomplished by two frequency modulated AC voltages, which offset $X+/X-$ and $Y+/Y-$ signals. The amplitude of the AC voltage varies the scanning size and frequency ratio between the AC voltage on X and Y controls the raster grid.

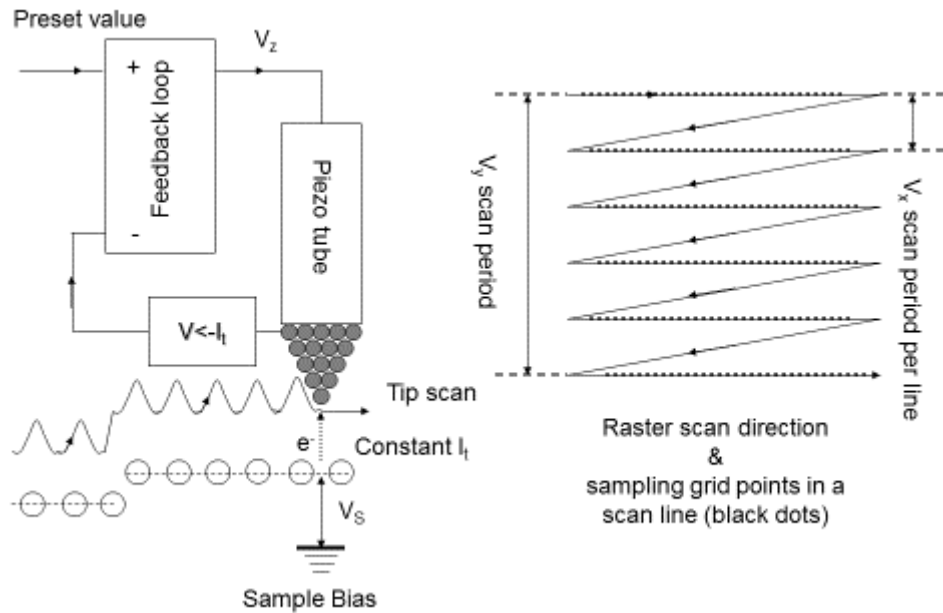


Figure 2.11 STM line scan and raster scan

During scanning, a biased voltage is applied on the specimen, and a frequency modulated I_t is amplified by a lock-in amplifier. The I_t is maintained at a value pre-set by the V_z through a feedback loop. As the tip scans at a height of several $\text{\AA}$ above the surface, the V_z value is converted into a tip height and the heights are recorded as an image of density of electron states. This is referred to the constant current mode. For its superior image quality and the tip safety, it widely replaces the constant height mode, which keeps V_z at a constant value and convert the varying I_t into an image.

Because the tip scans only several Å off from surface, the smallest vibration between the tip and the specimen can have a detrimental effect on the instrument. To minimize the vibrational effect on STM, the vibration isolation and the rigidity of STM body are of utmost importance in designing a STM chamber. The conventional method for vibration isolation is accomplished by either external pneumatic suspension or internal spring suspension. The external pneumatic suspension typically uses an airbed to support the entire UHV chamber including STM to isolate it from potential ambient vibration. The pneumatic pillars themselves provide the damping to any external vibration. For the internal spring suspension, it is chosen soft enough and its STM body is designed relatively heavy to lower resonance frequency away from the high frequency STM scan [36]. Additional damping mechanism such as Kepton wire or eddy current is usually integrated for noise suppression.

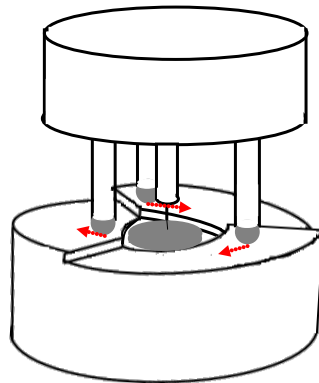


Figure 2.12 Beetle motor mechanism (Clockwise arrow - walk down; Counter-clockwise - walk up)

A tube scanner of STM can protract in length, but its travel distance is only in micrometers, too limited to provide enough clearance for introduction and removal of a sample. Thus a longer travel distance, such as for tip approach and full retraction, is required and a coarse approach motor is used.

In the two different STM systems used in this work, different motor mechanisms are utilized. The beetle motor (Fig. 2.12) in RHK STM uses three identical piezo tubes as an inertial walker style motor [36]. The piezo tubes stand on a smooth tri-ramp surface (made of polished TiN or Mo) and walk tangentially in a forward stroke followed by a backward stroke. In the forward stroke, the piezo tubes bend slowly to keep the friction against the ramp static, and the STM body rotates. In the following stroke, the piezo tubes bend back to the original stance fast enough that its friction is kinetic. In this case, the STM body barely rotates because its inertia is large, and little momentum impulse caused by the friction is transferred. Therefore, counter-clockwise or clockwise rotation moves the STM body up or down on the inclined tri-ramp. Such a motor mechanism is also termed as inertial walker.

In SPECS STM, the inch worm motor is configured with two identical co-axial tubes at the ends and a larger diameter tube in the middle (Fig. 2.13). Two tubes at the ends alternatively grip and release the STM support, and the larger tube extends or shrinks longitudinally between them to send the STM support up or down. For upward motion, the upper tube first shrinks to grip the STM support with the lower tube expanding to release the support (Fig. 2.13, Left). Then, the middle tube elongates to

move the lower tube to further down (Fig. 2.13, Middle). Next, the lower tube shrinks to grip the STM support while the upper tube releases it (Fig. 2.13, Right). After the middle tube contracts, the relative position of the STM support is translated by one stroke vertically up. The inch worm motor is ready for the next movement.

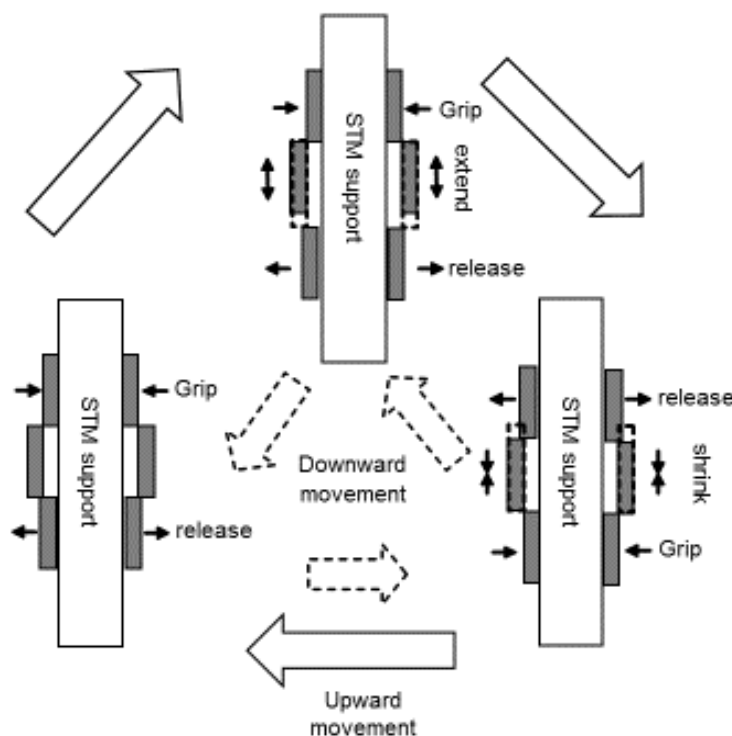


Figure 2.13 Sequential motions of an inch worm motor

The RHK beetle STM was tested prior to installing it into an UHV chamber. HOPG was used as a reference sample, and its (0001) surface was imaged in the air. For a large-area scan ($700 \text{ \AA} \times 700 \text{ \AA}$) in Fig. 2.14, STM images show C(0001) of HOPG step edge height $\sim 6.7 \text{ \AA}$, which corresponds to the lattice constant along [0001] direction for ABAB stacking. Close-up views of C(0001) clearly reveal the hexagonal lattice with

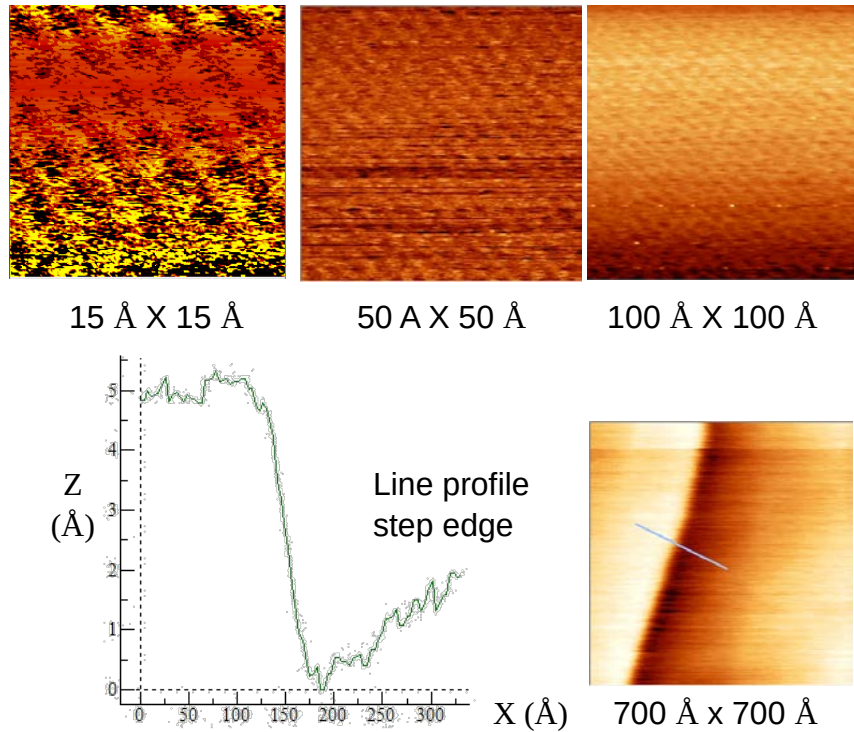


Figure 2.14 HOPG atomic resolution and step edge height

the measured lattice constant of 2.5 Å. The value is in excellent agreement with the expected value of 0.246 Å.

2.5.2 Low Energy Electron Diffraction (LEED) / Auger Electron Spectroscopy (AES)

LEED utilizes a fluorescent screen to visualize backscattered electron diffraction patterns from a surface. The incident electron beam of low energy (20-3000 eV) is emitted by an electron gun. Electrons are backward diffracted by the lattice of conducting crystal or a crystalline thin film on a conducting substrate. The backscattered electrons strike a fluorescent screen to illuminate the diffraction pattern. The elastically scattered electrons form sharp diffraction spots, and the inelastically scattered part forms smooth

background. To enhance the screen contrast, an extra potential over thousand volts is applied before the screen to further accelerate these electrons.

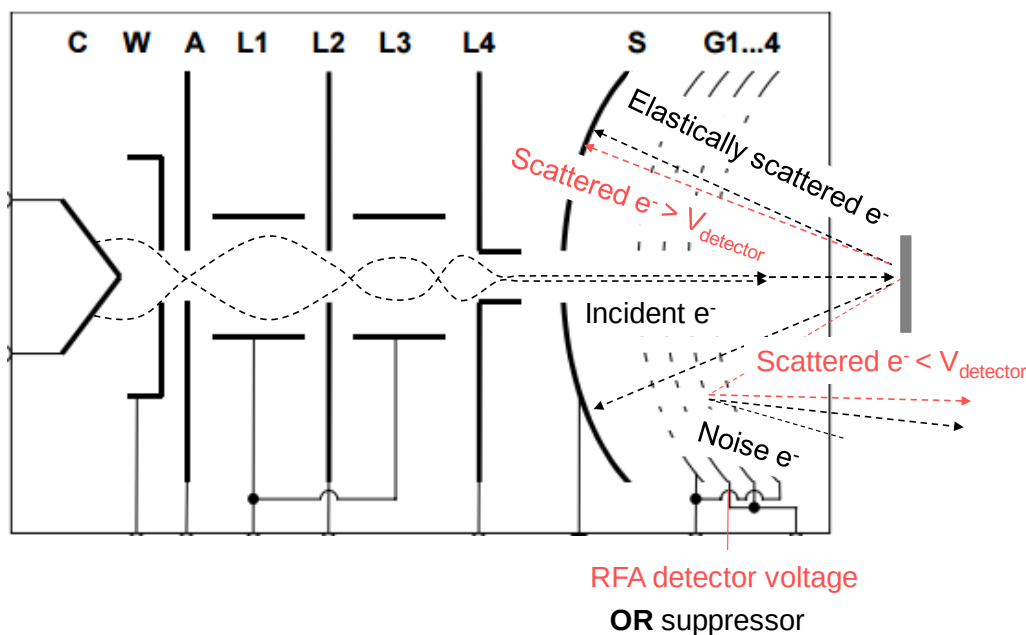


Figure 2.15 LEED/ AES optics (Black: LEED mode; Red: AES mode)

VSI LEED 150 used in this work is a reverse-view optics and its schematics is shown in Fig. 2.15. The whole LEED body of the LEED optics (electron gun, fluorescent screen, and grids) is mounted in a retractable linear feedthrough, right in front of the specimen for data acquisition. The electron beam is emitted by a LB_6 cathode in the electron gun. The thermal electrons are further accelerated by the anode potential set by the beam energy. Before the anode, electrons are electrostatically collimated by a negative biased Wehlnet cap with an aperture. Three elements of electrostatic lens: L1 and L3 (cylindrical lens pair, biased by a same signal), L2 (plate aperture), and L4 (drift

tube) are arranged coaxially. The electrons from the anode are electrostatically focused through L1, L2 and L3, and condensed into a beam. The L4 is simply a grounded drift tube acting as an outlet to remove the transverse oscillation. After back-scattered from a sample surface, the electrons travel through four concentric metal grids before hitting the screen. Two outer grids are grounded to provide a field-free region between the sample and the screen. Two inner grids are negatively biased to suppress the inelastically scattered electrons that contribute to the background intensity. Eventually, the filtered electrons are accelerated by screen voltage to produce the fluorescent diffraction pattern.

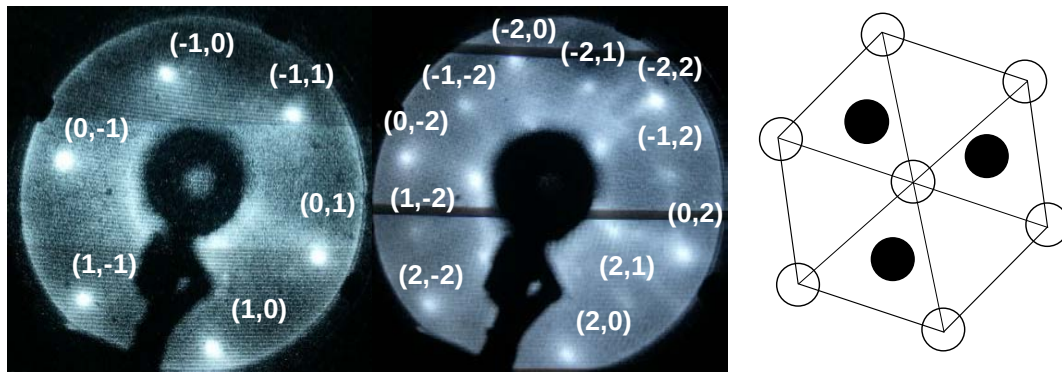


Figure 2.16 MoS₂(0001) LEED pattern at 100 eV, at 300 eV electron energy and the 2D atomic structure of (0001) surface (Black sphere: Mo, Open circle: S; Orientated as LEED pattern)

To test the LEED optics after installation, MoS₂(0001) has been used as a reference sample with the initial settings from the manufacturer's calibration report. Fig. 2.16 shows LEED diffraction patterns from MoS₂(0001) with 100 eV and 300 eV incident electron energies. At 100 eV, the first-order diffraction spots clearly reflect the

hexagonal symmetry of $\text{MoS}_2(0001)$. The specular beam (0, 0) is obscured from the view by the electron gun at the center of the optics. With increasing beam energy, the diffraction spots move toward the specular beam as the spot position represents the parallel component of the electron momentum. In addition, higher-order diffraction spots come into the field of view. Detailed explanation can be found elsewhere [37].

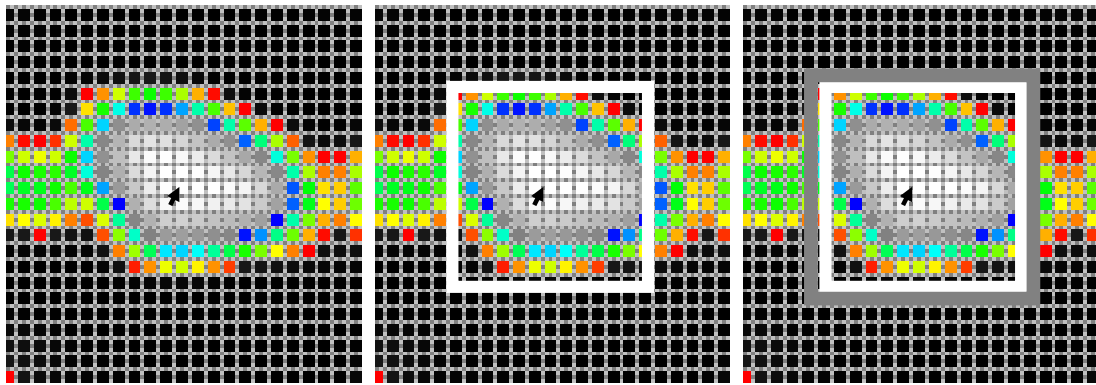


Figure 2.17 Auto search of spot size and background subtraction - (1,1) spot from rutile (1x1) $\text{TiO}_2(110)$ at 140 eV (Left- maximum intensity pixel of spot, middle-spot size right-background box search)

The intensity analysis of diffraction spots can provide structural information of the surface, also known as the spot profile analysis of LEED (SPALEED) [38-42]. The intensity versus voltage curves or simply I-V curves of diffraction spots need to be measured over a wide energy range. In this dissertation, a WATEC 902C low intensity camera is used to record LEED images as 8-bit bitmap picture. The I-V curves are then extracted by LEED Analysis I-V Extractor (LANSIVE) program written in Labview [37]. Before they can be used for structural calculation and simulation, the background intensity in the I-V curves must be accurately estimated and subtracted. A background

subtraction function employs an auto search for the correct spot size (Fig. 2.17). The auto search first searches the pixel location of the maximum intensity (black arrow) in a diffraction spot. Then, it keeps expanding a square frame of pixels (white square frame) centered at the maximum intensity pixel using a user-defined initial size. The average intensity of pixels on the square boundary line is compared to that on the larger, subsequent frame (gray square frame) in next search step. When the averaged intensity boundary line is less than or equal to that on the subsequent boundaries, it is assumed the “correct” size is found. Then, the average intensity of the pixels within the spot boundary is regarded as the intensity of the diffraction spot, and that of the boundary line is regarded as background intensity. The calibrated intensity of the diffraction spot is obtained after the background intensity is subtracted from the spot intensity.

The LEED optics can be also used as an electron spectrometer for Auger electron spectroscopy (AES), which can be used to identify elemental information of the specimen [32]. In the Auger process, high energy electrons (3 – 5 kV) excite a core-level electron of an atom, creating a core hole. The core hole is sequentially filled by an outer shell electron. The binding energy difference between the core level (E_B) and the outer shell (E_1) is transferred to kick off another electron from an outer shell (E_2). This electron, also known as Auger electron, carries the energy $E_{\text{Auger}} = E_B - E_1 - E_2$, which is unique to the electronic structure of the atom. These electrons appear as a peak or bump in the electron distribution curve (EDC).

In the AES mode, four grids and fluorescent screen together function as a retarded field analyzer (RFA). Only the electrons with sufficiently high energy can overcome the electrical potential applied over two inner grids at the AES energy. A positive bias (~ 500 V) is further applied on the screen to prevent charging of electrons. The electron current from the screen is proportional to the number of electrons with energy higher than the potential of the inner grids. By subtracting between two signals with energy difference of a scan step, the electron current spectrum $N(E)$ can be obtained. A lock-in amplifier modulates the screen voltage in high frequency AC offset (~ 1 kHz) so that the background can be filtered out.

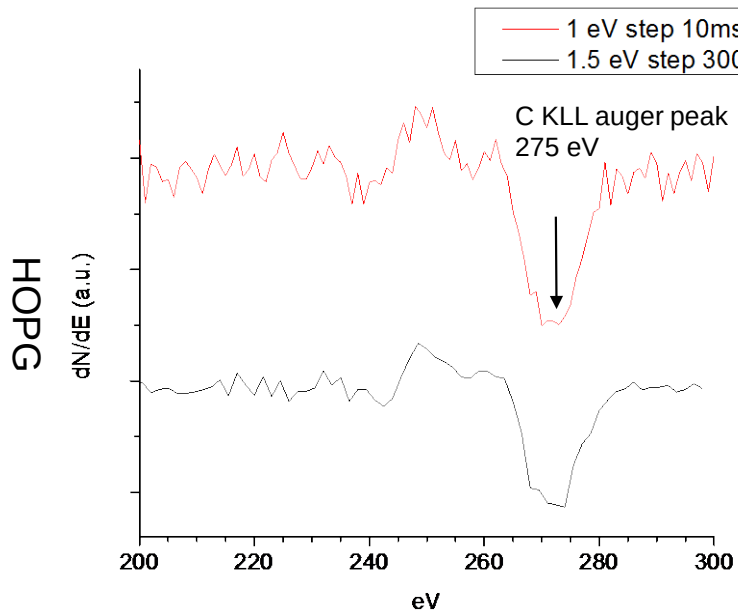


Figure 2.18 HOPG test result and comparison to published data

To test the AES mode of the LEED optics, HOPG and Au foil have been used. Various energy steps and signal integration time for RFA have been used to test the

energy resolution. In Fig. 2.18, the AES curves of HOPG are presented with two different RFA settings: (1) energy increment of 1 eV with integration time of 10 ms and (2) the energy increment of 1.5 eV with the increment of 300 ms. Both data show a strong peak at 275 eV, which is consistent with the carbon KLL Auger peak from the data of AES handbook [43]. The KLL Auger transition represents the excitation of a L-level electron caused by the energy gained from the transition from a L-level electron to K-level core hole. The advantage of a longer time for signal integration such as 300 ms is that it can effectively average out the background noise without sacrificing energy resolution.

In Fig. 2.19, the AES curves from an Au foil are recorded with different energy steps with 200 ms integration time to test the energy resolution of Au Auger peaks. A visual comparison of Auger spectra with various energy steps from 0.2 to 1 eV demonstrates that the smaller energy step of 0.2 eV yields best resolution for peaks

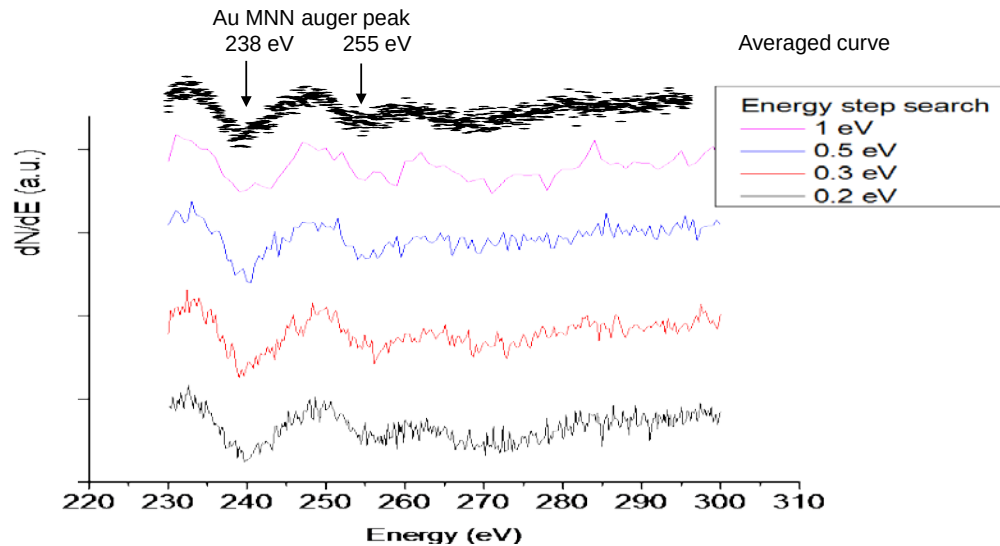


Figure 2.19 Au foil AES test result and comparison to published data

at 238 eV and 255 eV. They are both identified as Au MNN auger peaks. On the other hand, the spectrum with the large energy step of 1 eV shows much smaller noise (less scattered data points), but in the lowest energy resolution.

2.6 Design and Construction of an UHV System for Tip-enhanced Raman Spectroscopy (TERS)

2.6.1 Integration of RHK STM and LSAM LEED Systems

Raman uses electromagnetic wave of a laser to excite the unique vibrational modes of different molecules or crystal, and the excitation signature in the spectrum can provide chemical and elemental information. Its spatial resolution is limited ultimately to the diffraction limit, typically hundreds of nanometer. On the other hand, STM images surface topography, more precisely, density of electron states in atomic resolution. However, chemical or elemental information is not typically available. TERS combines STM and Raman to take advantage of the strengths in both techniques. In TERS, a sharp STM tip not only provides an atomic-scale spatial resolution, but also the enormous electric field due to the sharpness of the tip and its proximity to a surface. As the Raman intensity is proportional to the square of the field strength, the Raman signal under the tip area can be dramatically enhanced for detection. Such *in situ* capability to identify and map in nanometer scale would be powerful and highly valuable.

To set up TERS, two existing UHV systems of RHK beetle STM and LSAM LEED in Baylor Science Building had to be combined first and then further integrated with the

optical system for Raman spectroscopy in Baylor Research and Innovation Center (BRIC). Moreover, it was essential to design custom adaption parts for their combined functionality. This section describes the system integration and modification in the STM and LEED chambers.

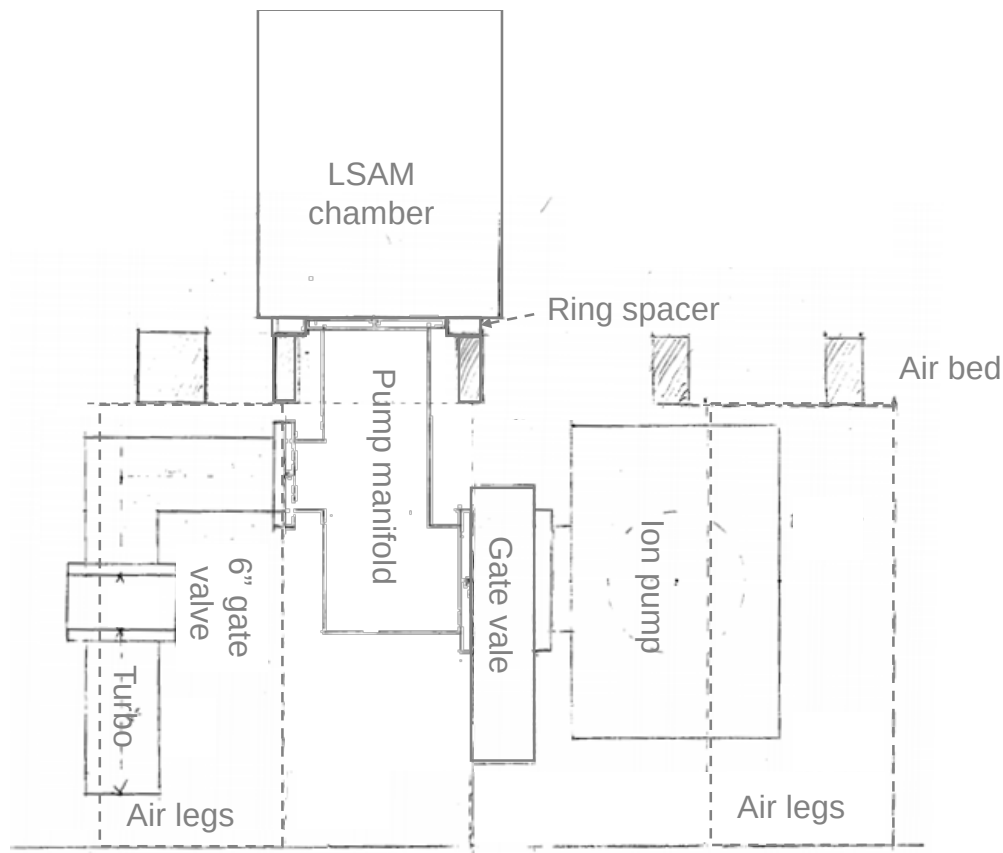


Figure 2.20 Custom design pumping manifold and chamber alignment

The first step of the integration is to install the LEED chamber from LSAM onto the vibration isolation platform so that it can be later connected to the STM chamber. For a coarse alignment between two chambers, an aluminum ring spacer (8.1 inch inner, 12 outer diameter, 1 inch thickness) is machined and inserted under the LEED chamber to

raise it. For a fine alignment, the STM chamber is nut-mounted on four 3/8 inch threaded supporting rods. The level and height of STM chamber can be precisely controlled by adjusting mounting nuts (Fig. 2.20). Next, a pumping manifold is designed and installed underneath the LEED chamber so that the ion pump, the main turbo pump and the gate valves can be isolated from the floor as well. The manifold is also designed to ensure an enough clearance against ground in the movement of the airbed. The unbalance weight due to the ion pump and the turbo pump causes significant torque on the bottom flange of LEED chamber. To alleviate the problem and prevent any permanent damages, steel girders and threaded rods are nut-mounted together to suspend the ion pump and the main turbo pump.

2.6.2 New Design of Sample Stage-holder and Sample Transfer between the STM and LEED Chambers

The RHK beetle STM and the LSAM LEED chamber originally employed different sample holder/ stage designs. Therefore, the integration of the two systems required a new design modification for the sample holder/ stage. Because the design of the RHK holder is essential to STM operation (Fig. 2.21), the sample stage in the LEED chamber (Fig. 2.22) is modified to accept the STM sample holder.

The top of the RHK holder is made as a TiN or Mo tri-ramp by which the STM legs are supported. The base is made with Cu for sample insertion and manipulation. The track between the upper two rings on the periphery of the holder is to fit a fork-shaped wobble stick. The lower track is designed for the holder insertion to a spring compressed

retainer. A central hole is bored through for a retractable filament heater to approach the specimen from the beneath.

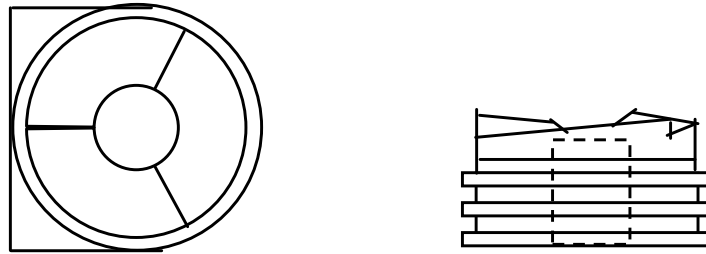


Figure 2.21 RHK sample holder

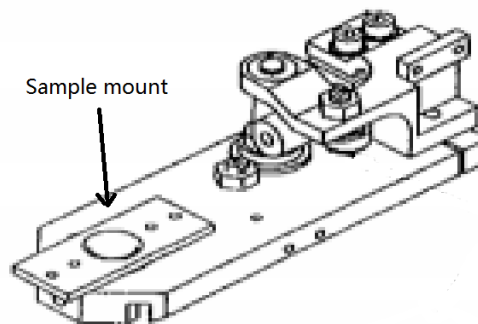


Figure 2.22 SH2 Sample stage

The SH2 sample stage is designed for Angle Resolved X-ray Photoemission Spectroscopy (ARXPS) with a gear-belt driven, rotatable sample mount. The ceramic track thermally and electrically isolates the sample mount (Fig. 2.22), the use of sapphire bearing allows its rotation while keeping the mount isolated. A center hole in the sample stage can be used to mount a fixed e-beam heating filament for specimen heating. The SH2 sample stage is redesigned with the following three major goals. 1. The insertion and retraction of the RHK sample holder can be easily achieved; 2. The heating filament can

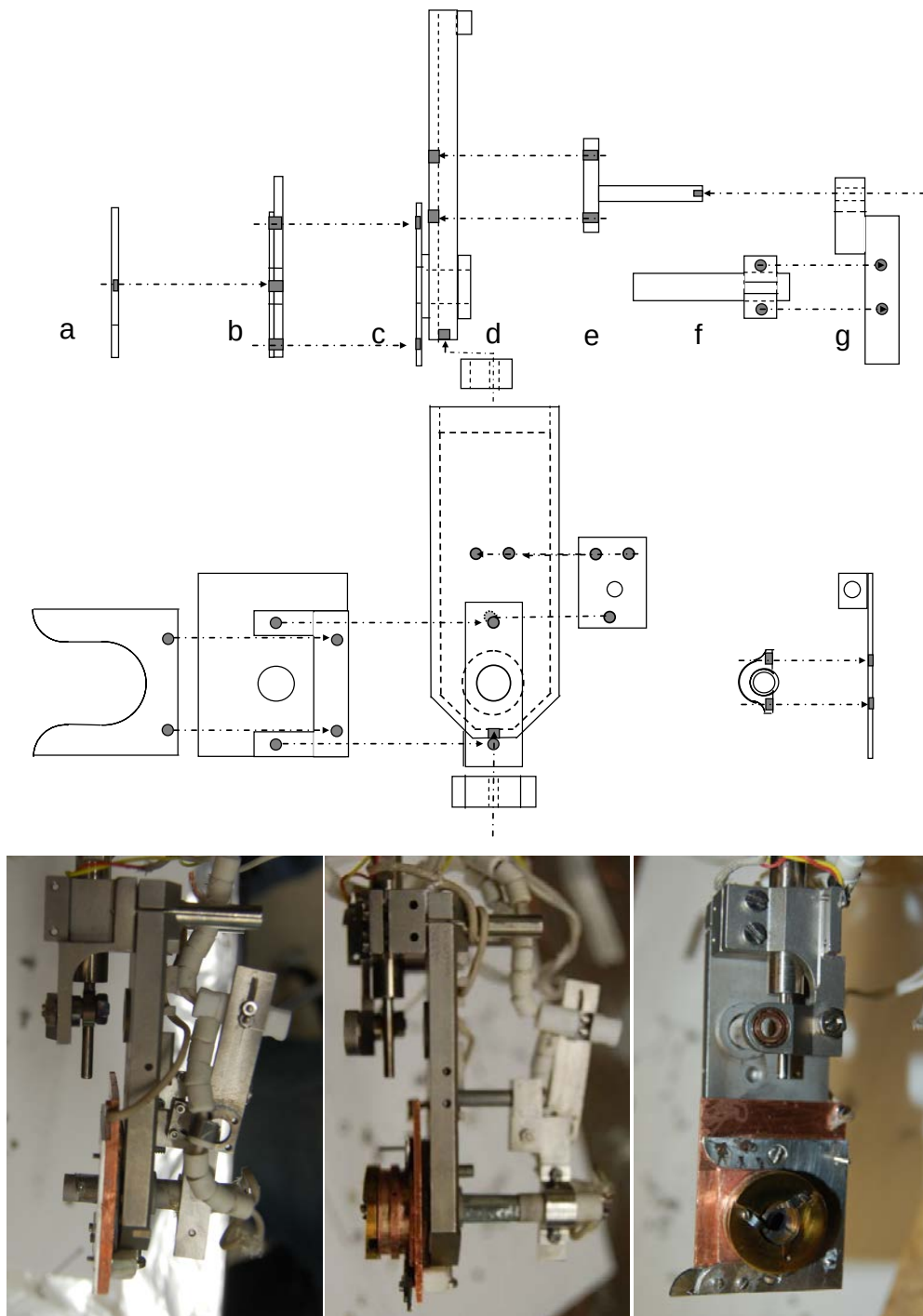


Figure 2.23 Sample stage design, assembly layout (Higher) and images of sample stage (Lower) (Higher: Slash and dotted arrow - nut mounting direction; Gray area - threaded hole; Lower: Left - side view w/o holder; middle - side view w/ holder; Right- front view w/ holder)

be moved out of the center hole when the RHK holder needs to be mounted; 3. The sample holder remains thermally and electrically isolated. A new custom-made sample holder is shown in Fig 2.23. A U-shaped spring plate is made of stainless steel 304 (SS 304, Fig. 2.23a) and is bolted on a machined copper base (Fig. 2.23b) with a U-shaped stage (1 mm height). When the RHK sample holder is inserted or extracted, the spring plate grabs the holder, and the copper stage provides a clearance for the holder base to slide in and out. The copper base is bolted onto the rotatable sample mount of the SH2 specimen stage (Fig. 2.23c). Since the SH2 sample mount is thermally isolated, it can easily accommodate cryogenic cooling cap with a LN2 reservoir connection in future. A Macor constraint (Fig. 2.23d) is bolted under the SH2 stage to limit the rotation. Because of Macor used in design, the specimen remains electrically and thermally isolated [44]. A rod shaft with its rectangular base (Fig. 2.23e) is bolted on the back of SH2 stage. A conformal fastener (SS 304) is used to attach the heater assembly (Fig. 2.23f) on its support (SS 304, Fig. 2.23g). The shaft mount (SS 304, bolted on shaft support) can slide together with the heater using a wobble stick. When the heater is in position through the hole of the copper base, it can be used to heat the specimen. After heater is retracted below, the sample holder can be removed safely.

The custom designed heater assembly is shown in Fig. 2.24. The heater body is combined by a machined Macor tube spacer (a) and an alumina ring (b). Their outer diameter is 8.6 mm so that the heater assembly can be inserted and retracted through the center hole of the redesigned stage. Three through hole with the same diameters are

drilled in the tube spacer. Two diagonally positioned holes are for mounting two miniature size steel tubes (d). The steel tubes hold filament legs (W wire, e). Another hole is off-set drilled for pumping trapped gases. The alumina ring is for housing the the hot filament and isolating high voltage and high temperature. The throriated tungsten filament is mounted on the support tungsten wire (e) and the tungsten wire is clamped by the steel tubes. The 0.025 inch diameter filament (c) is manually wound into a coil. This design makes sure that heat form filament is conducted through increasing cross section of filament wire, tungsten wire and steel tubes. At the same time, the design allows sufficient rigidity and reliability for heating operation at high temperature. After filament, supports and steel tubes (c, d and e) are assembled into the tube spacer, the alumina ring houses outside of the filament. The whole assembly is glued together using UHV compatible Armco ceramic adhesive 516.

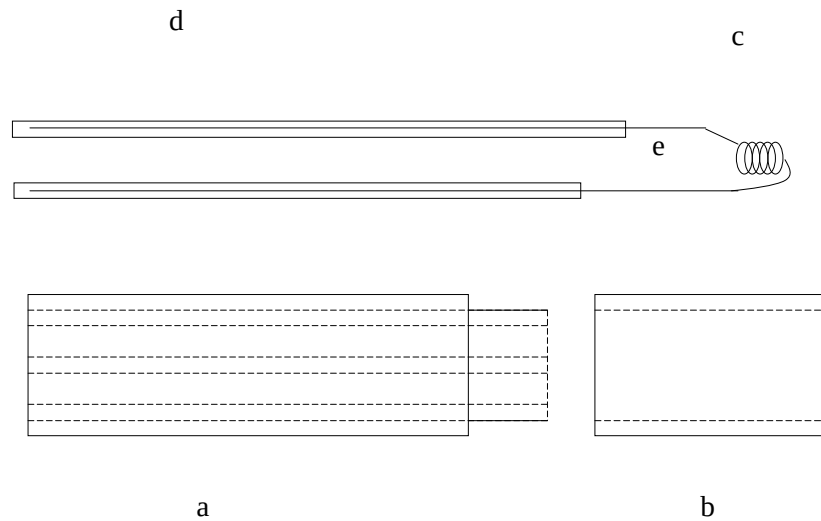


Figure 2.24 Heater assembly design

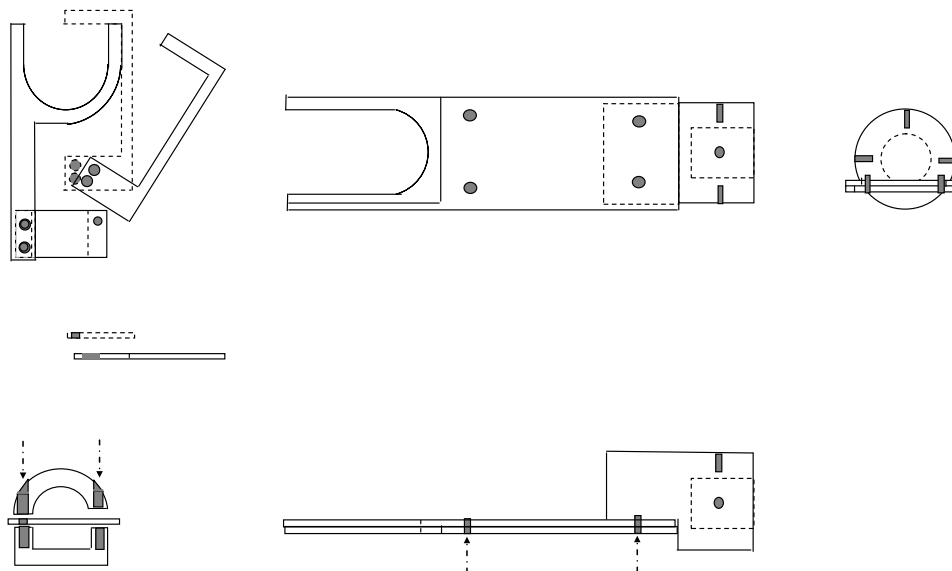


Figure 2.25 Sample fork with securing lock for wobble stick and load lock

The RHK holder is horizontally mounted in STM chamber whereas SH2 stage is designed for vertical sample mounting. A rotatable wobble stick is therefore installed on the LEED chamber for the transition between the two mounting orientations. In addition, the SH2 stage has limited space in its upper area (see Fig. 2.22), requiring horizontal insertion and extraction of RHK holder. In order to meet the requirement, a lock function has to be implemented in the custom-designed fork for holder manipulation, as an add-on part on the wobble stick. A right angled lock (Fig. 2.25, Left, SS 304 machined) is bolt-mounted on the clamp of the wobble stick. When the lock is closed to secure the holder, the wobble stick can safely pull the sample hold out. The fork is bolt-mounted by two steel clamps (Fig. 2.25, Left) and fastened by its friction on the wobble stick body.

The upper clamp is horizontally machined off for 1 mm on one side. It can maximize the fastening force from the tightened mounting bolts with an improved reliability.

The combined TERS chamber utilizes two transfer arms for the transition between the LEED and the RHK chamber as well as the fast entry load-lock. To transfer the RHK sample holder using the transfer arm, another sample fork is designed (Fig 2.25, Right). The fork is machined from stainless steel 304 plate, and the tips in the arms of the fork are slightly bended inward to retain the holder for minimizing possibility of holder dropping. A underneath plate with a constraint arm is designed to limit possible rotation of holder. To connect the fork on the transfer arm, a cylinder is off-centered cut for bolt-mounting so that the clearance between the sample holder and the inner wall of transfer arm is maximized. On the other side of the cylinder, a hole is bored for bolt-mounting it onto the transfer arm.

The wobble stick used to mount the sample in the LEED chamber has a long travel-distance, and protruding substantially outside the chamber. Because of the protrusion, unexpected bumps may damage its bellows and the seal to the UHV chamber. To protect the bellows and provide a resting position, a custom-designed lock is made as shown in Fig. 2.26. Two adaptors (Fig. 2.26A & B) are machined from 1 inch thick aluminum plate. They are connected by a threaded steel rod, and two nut retainers can adjust the position of B to which the insertion depth of wobble stick beyond the chamber wall is limited. When the chamber is under UHV, atmosphere pressure pulls wobble stick toward the chamber, and the unbalanced handle is pulled downward by its weight. The

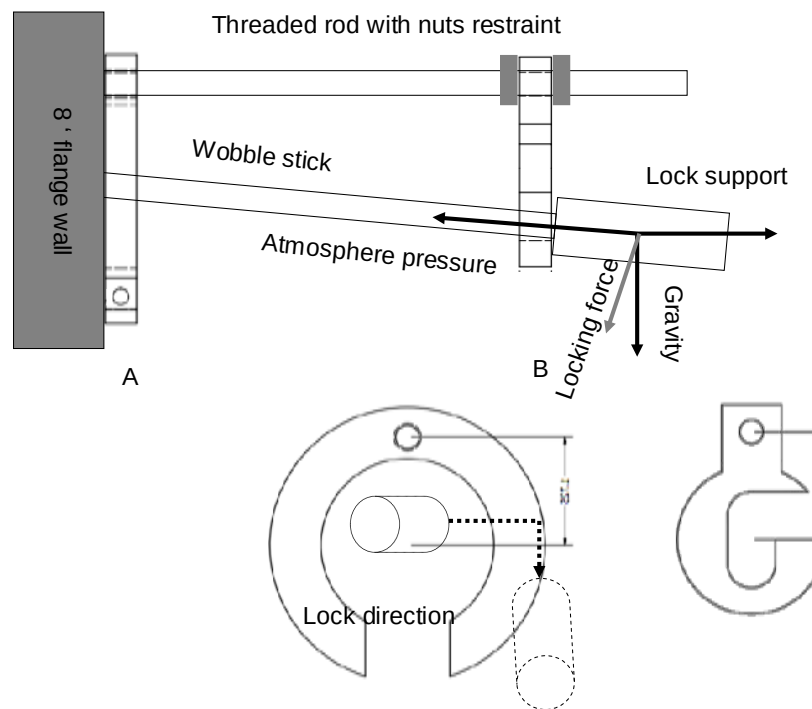


Figure 2.26 Wobble stick lock for LEED chamber

handle can be therefore locked inside the slot of B. When the adaptor A is pushed against flange wall by vacuum, the lock can limit its insertion depth to a safe distance.

2.6.3 Calibration and Testing of the TERS system

Fig. 2.27 shows the fully assembled TERS UHV chamber in BRIC. For the initial testing, copper phthalocyanine (CuPc) is deposited on Ag(111) surface using thermal evaporation. The chemically inert CuPc is self-arranged and assembled on Ag(111) [37]. A monolayer of molecule can be formed after desorbing excess molecules from the surface.

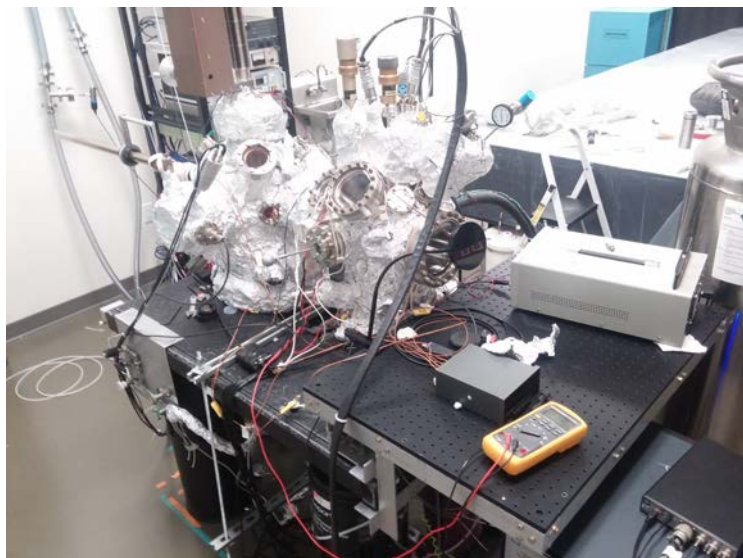
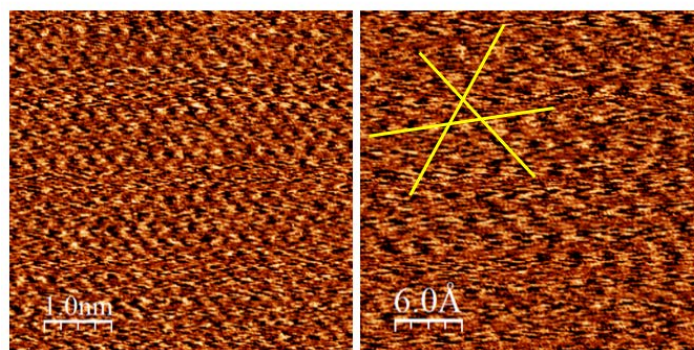


Figure 2.27 TERS chamber after completion

Atomic resolution of Ag (111)



Molecular resolution of
CuPc mono layer on Ag (111)

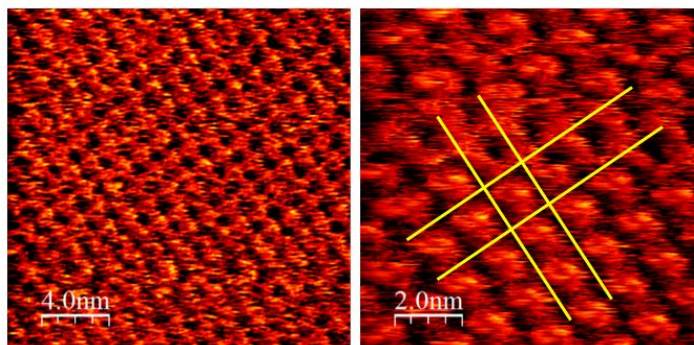


Figure 2.28 Atomic resolution of Ag(111) and molecular resolution of CuPc mono layer evaporated on Ag(111)

Fig. 2.28 shows an atomically resolved Ag(111). The surface lattice vectors forms a hexagonal lattice with $a = b = 2.9 \text{ \AA}$ and $\theta = 120^\circ$ as expected from the (111) surface of face-center cubic Ag. After CuPc deposition and annealing, the molecular resolution of CuPc monolayer has been imaged on Ag(111) (Fig. 2.28, lower). A much larger surface unit cell of rectangular symmetry with a lattice constant $\sim 14.6 \text{ \AA}$ can be identified. The value is consistent with those reported in literature [37] and is shown by yellow lines (Fig. 2.28, Lower right).



Figure 2.29 Ag(111) LEED pattern and surface atomic structure (Left - Ag(111) LEED pattern at 84.5 eV; Middle - Ag LEED at 189.5 eV; Right - Ag(111) surface atomic structure)

A LEED pattern of clean Ag(111) is shown in Fig. 2.29. It shows that the diffraction spots in hexagonal symmetry consistent with the hexagonal geometry of Ag(111) 2D surface lattice (Fig. 2.29, right). They move toward the center of screen, and the higher order spots appear as the beam energy increase (Left to middle).

The AES spectra taken from Ag(111) and the CuPc deposited surface are shown in Fig. 2.30. For Ag surface (Fig. 2.30, lower black curve), the spectrum reveals the

distinctive MNN auger peaks of Ag at 260, 266, 351 and 356 eV (Black arrows) [43]. After CuPc deposition onto Ag(111) (Fig. 2.30, higher red curve), the MNN peaks of Ag at 351 and 356 eV can be observed. However, its weaker MNN peaks at 260 and 266 eV are buried under the background whereas a KLL auger peak of carbon

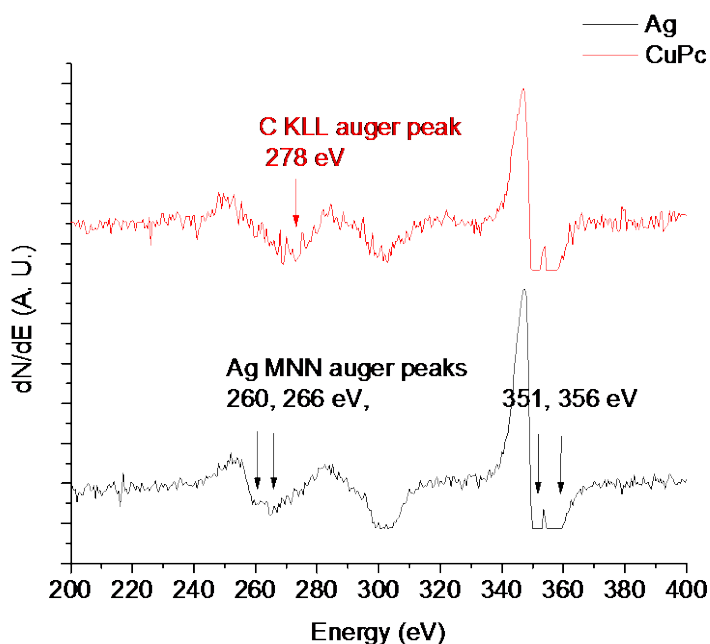


Figure 2.30 AES- Clean Ag(111) (lower) and CuPc deposition on Ag (upper)

at 278 eV emerges nearby (red arrow). The intensity attenuation of the Ag peaks is caused by the surface coverage of CuPc, the intensity of the electrons exponentially decays due to inelastic scattering as they pass through the overlayer.

CHAPTER THREE

Theory

3.1 Principle of Quantum Tunneling in STM

The simplest model illustrating the tunneling effect of an electron between a STM tip and a sample uses a potential barrier and the quantum transmission problem of a plane wave [36]. As shown in Fig. 3.1, it is supposed that the plane wave of an electron with the kinetic energy E travels along the z direction, and encounters a rectangular potential barrier of height V ($V > E$), representing the vacuum energy. Classically, the plane wave cannot penetrate the barrier because $V > E$. However in quantum mechanics, the Schrödinger equation gives a solution for which the plane wave function exponentially decays through

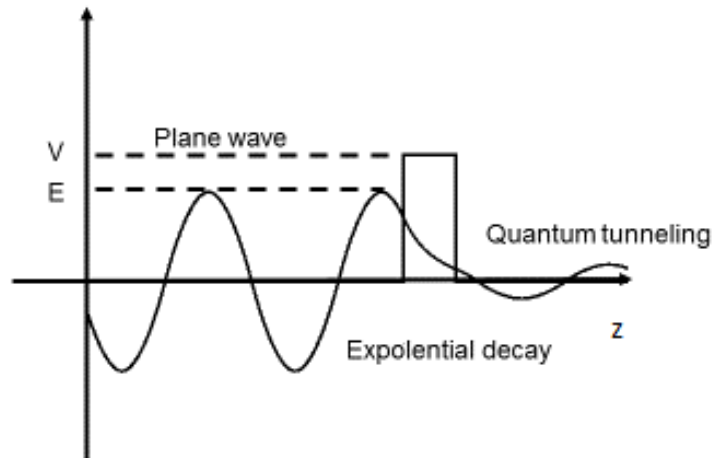


Figure 3.1 Quantum tunneling

the potential barrier. The electron is tunneling through vacuum between the sample and the tip. STM uses this principle to probe electron density over the sample surface.

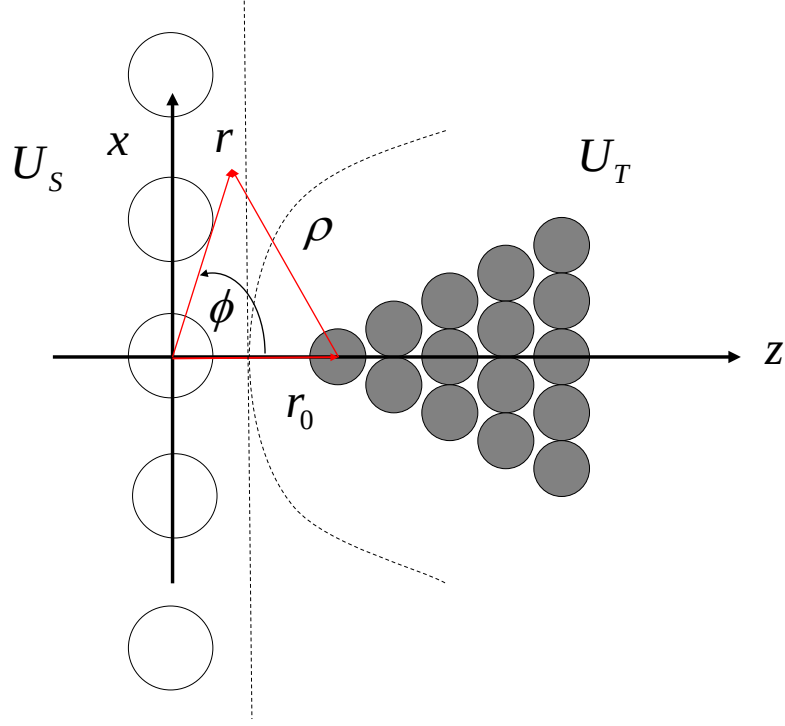


Figure 3.2 Potential model of sample and tip

A more rigorous treatment of the tunneling phenomena can be found in many books. In this section, the STM tunneling model by C. Julian Chen [36] is briefly reviewed for a background introduction. Then, the model will be applied to $\text{TiO}_2(110)$. In Fig. 3.2, the spatial vector is taken as r and the center of apex atom in the tip is taken as r_0 . The surface is along the x direction, and the z direction points into the tip. Non-overlapping potentials of the sample and the tip are defined as U_s and U_T , respectively, via time-dependent perturbation methods. The time that interaction takes place is denoted as t .

When $t < 0$, the free tip potential U_{T_0} is lowered to U_T allowing electrons to tunnel into the sample. When $t > 0$, U_T is turned off and the free sample potential U_{S_0} is lowered to U_S for accepting the electrons. So we have:

$$U = U_S + U_T \quad (3.1)$$

and

$$U_S U_T = 0. \quad (3.2)$$

The energy eigenstate of surface electrons φ_μ are given by the Schrödinger equation with the kinetic energy operator, $T = -(\hbar^2 / 2m)\nabla^2$:

$$(T + U_S)\varphi_\mu = E_\mu \varphi_\mu. \quad (3.3)$$

The energy eigenstate of tip electrons χ_ν is given by:

$$(T + U_T)\chi_\nu = E_\nu \chi_\nu. \quad (3.4)$$

To calculate the electron transition rate from the tip to the sample, we can use a time dependent Schrödinger equation for wave function ψ and treat the tip potential U_T as perturbation:

$$i\hbar \frac{\partial}{\partial t} \psi = (T + U_T + U_S)\psi. \quad (3.5)$$

The wave function ψ can be expanded in terms of the tip electron states χ_ν :

$$\psi = \sum_\nu a_\nu(t) \chi_\nu e^{-iE_\nu t/\hbar}. \quad (3.6)$$

When $t = 0$, the time dependent expansion constant can be written as:

$$a_\nu(t) = (\chi_\nu, \psi_\mu) e^{-i(E_\mu - E_\nu)t/\hbar} + c_\nu(t) \quad (3.7)$$

in which (χ_ν, ψ_μ) is the inner product and $c_\nu(0) = 0$. Then, we can have:

$$\Psi = \psi_\mu e^{-iE_\mu t/\hbar} + \sum_\nu c_\nu(t) \chi_\nu e^{-iE_\nu t/\hbar} . \quad (3.8)$$

Substituting Eq. 3.8 in Eq.3.5, the equation for $c_\nu(t)$ can be obtained:

$$i \dot{c}_\nu(t) = (\chi_\nu, U_T \psi_\mu) e^{-iE_\mu t/\hbar} + \sum_\lambda c_\lambda(t) (\chi_\nu, U_s \psi_\lambda) \chi_\lambda e^{-iE_\lambda t/\hbar} . \quad (3.9)$$

The transition probability from the electron state χ_ν to the state ψ_μ in first-order perturbation theory is given by Fermi's golden rule:

$$\omega_{\nu\mu}^{(1)} = \frac{2\pi}{\hbar} |M_{\nu\mu}|^2 \delta(E_\mu - E_\nu) \quad (3.10)$$

with the transition matrix as an volume integral in the tip space Ω_τ :

$$M_{\nu\mu} = \int_{\Omega_\tau} \psi_\mu^* U_T \chi_\nu d\tau . \quad (3.11)$$

Because of the delta function in Eq. 3.10, we require the transition is elastic that $E_\mu = E_\nu$.

As the integral over the tip, there is no sample potential U_s so that we can have

$T\varphi_\mu = E_\mu\varphi_\mu = E_\nu\varphi_\mu$ from Eq. 3.3. By using this identity, the matrix elements can be

rewritten as:

$$\begin{aligned} M_{\nu\mu} &= \int_{\Omega_\tau} \psi_\mu^* U_T \chi_\nu d\tau \\ &= \int_{\Omega_\tau} \psi_\mu^* (E_\nu - T) \chi_\nu d\tau \\ &= \int_{\Omega_\tau} E_\mu \psi_\mu^* \chi_\nu - \psi_\mu^* T \chi_\nu d\tau \\ &= \int_{\Omega_\tau} T \psi_\mu^* \chi_\nu - \psi_\mu^* T \chi_\nu d\tau \\ &= \int_{\Omega_\tau} (\chi_\nu T \psi_\mu^* - \psi_\mu^* T \chi_\nu) d\tau . \end{aligned} \quad (3.12)$$

Eq. 3.12 can be transformed to the surface integral by Green's theorem:

$$M_{\nu\mu} = \frac{\hbar^2}{2m} \int_\Sigma (\psi_\mu^* \nabla \chi_\nu - \chi_\nu \nabla \psi_\mu^*) \cdot dS . \quad (3.13)$$

In order to calculate transition matrix $M_{\nu\mu}$, we need both wave functions of the tip and the sample. The tip wave function is given by Schrödinger's equation in the vacuum, which is only valid near the separation surface between the tip and sample. The sample wave function also shares the same equation with $\rho = |r - r_0|$ because of the elastic transition:

$$[\nabla^2 - \kappa^2]\chi(\rho) = 0 \quad (3.13)$$

and $\kappa = (2m\Phi)^{\frac{1}{2}}\hbar^{-1}$ where Φ is the work function of the tip.

The solution can be written as a sum over expansion terms in l and m of the spherical-harmonics $Y_{lm}(\theta, \phi)$, the expansion coefficient C_{lm} and radial component $f_{lm}(\kappa\rho)$:

$$\chi(\rho) = \sum_{l,m} C_{lm} f_{lm}(\kappa\rho) Y_{lm}(\theta, \phi). \quad (3.14)$$

The radial solution $f_{lm}(\kappa\rho)$ can be written as spherical modified Bessel functions of first or second kind, i_l or k_l . But i_l cannot be used because of its divergence at large radius.

The expansion term of solution should be only with k_l terms that:

$$\chi_{lm}(\rho) = C_{lm} k_l(\kappa\rho) Y_{lm}(\theta, \phi). \quad (3.15)$$

In STM experiment, a typical tungsten tip provides a dominant d state electrons in the conduction band minimum when scanning TiO_2 surface. The d state electrons are tunneling to s or d empty states of the Ti^{4+} ions of the sample surface. Such tunneling condition requires $l = 2$ for tip electron state and $l = 0$ or 2 for the sample electron state. Furthermore when $m \neq 0$, the angular distribution component of the wave function,

$Y_{lm}(\theta, \phi)$, creates separated lobes in the ϕ plane, and these lobes in the electron wave could be limiting factors in STM resolution. For simplicity, the tip and sample electron states in $m=0$ states: s state electron of the sample and d_{z^2} state of the tip are considered. Then, we have wave function χ_{00} and χ_{20} for the tip:

$$\chi_{00} = C \frac{1}{\kappa \rho} e^{-\kappa \rho} \quad (3.16)$$

$$\chi_{20} = C \left[\frac{1}{\kappa \rho} + \frac{3}{(\kappa \rho)^2} + \frac{3}{(\kappa \rho)^3} \right] \frac{1}{\kappa \rho} e^{-\kappa \rho} \left(\cos^2 \theta - \frac{1}{3} \right). \quad (3.17)$$

In order to calculate the transition matrix, we utilize Green's function for the modified Helmholtz equation (Eq. 3.13.) which is defined by the following differential equation:

$$[\nabla^2 - \kappa^2]G(r - r_0) = -\delta(r - r_0). \quad (3.18)$$

The solution at the boundary condition that $G(r - r_0)$ remains regular when $|r - r_0| \rightarrow \infty$ is

$$G(r - r_0) = \frac{\exp(-\kappa |r - r_0|)}{4\pi |r - r_0|}. \quad (3.19)$$

Its solution can be written as modified Bessel function of the second kind k_i :

$$G(r - r_0) = \frac{\kappa}{4\pi} k_0(\kappa \rho). \quad (3.20)$$

By utilizing the differential relation of k_i :

$$\frac{d}{du} k_0(u) = -k_1(u) \quad (3.21)$$

and taking the derivative of Eq. 3.20 with respect to the height of the apex atom in the tip

z_0 , we can get:

$$\frac{\partial}{\kappa \partial z_0} G(r-r_0) = \frac{\kappa}{4\pi} \frac{z-z_0}{\rho} k_1(\kappa\rho). \quad (3.22)$$

Then we take the second derivative of Eq. 3.22 by recognizing

$$\frac{3k_1(u)}{u} = k_0(u) - k_2(u). \quad (3.23)$$

This yields:

$$\frac{\partial^2}{\kappa^2 \partial z_0^2} G(r-r_0) = \frac{\kappa}{4\pi} \left(\frac{(z-z_0)^2}{\rho^2} k_2(\kappa\rho) - \frac{1}{\rho} k_1(\kappa\rho) \right). \quad (3.24)$$

Now, we can write the d_{z^2} state wave function Eq. 3.17 as:

$$\chi_{dz^2} = \frac{4\pi C}{\kappa} \left(\frac{\partial^2}{\kappa^2 \partial z_0^2} G(r-r_0) - \frac{1}{3} G(r-r_0) \right). \quad (3.25)$$

Keeping in mind that the sample state function $\psi(r)$ is a real function and obeys the same equation of motion Eq. 3.13, the matrix element M may be evaluated using Eq. 3.13, 3.18, 3.19 and 3.25:

$$\begin{aligned} M_{d_{z^2}} &= -(\hbar^2 / 2m) \frac{4\pi C}{\kappa} \left(\frac{\partial^2}{\kappa^2 \partial z_0^2} - \frac{1}{3} \right) \int_{\Sigma} [G(r-r_0) \nabla \psi - \psi \nabla G(r-r_0)] dS \\ &= -\frac{2\pi \hbar^2 C}{\kappa m} \left(\frac{\partial^2}{\kappa^2 \partial z_0^2} - \frac{1}{3} \right) \int_{\Omega} [G(r-r_0) \nabla^2 \psi - \psi \nabla^2 G(r-r_0)] d\tau \\ &= -\frac{2\pi \hbar^2 C}{\kappa m} \left(\frac{\partial^2}{\kappa^2 \partial z_0^2} - \frac{1}{3} \right) \int_{\Omega} \psi \delta(r-r_0) d\tau \\ &= -\frac{2\pi \hbar^2 C}{\kappa m} \left(\frac{\partial^2}{\kappa^2 \partial z_0^2} - \frac{1}{3} \right) \psi(r_0). \end{aligned} \quad (3.26)$$

From the transition matrix element, the tunneling current can be calculated as an energy integral over all available transition electrons in both the tip and sample with the approximation that $k_B T$ is small:

$$\begin{aligned}
I &= \frac{4\pi e}{\hbar} \int_{-\infty}^{\infty} [f(E_F - eV + \epsilon) - f(E_F + \epsilon)] \rho_S(E_F + \epsilon) \rho_T(E_F - eV + \epsilon) |M|^2 d\epsilon \\
&= \frac{4\pi e}{\hbar} \int_0^{eV} \rho_S(E_F + \epsilon) \rho_T(E_F - eV + \epsilon) |M|^2 d\epsilon
\end{aligned} \tag{3.27}$$

where $f(E) = \{1 + e^{[(E-E_F)/k_B T]}\}^{-1}$ is Fermi distribution function, and ρ_S / ρ_T are the density of states in the sample/ tip surface.

In a constant current STM mode used in this work, the tunneling current I is kept at a set value I , and the tip protracts and retracts to follow the sample surface. With z as the height of tip and X as tip position vector in the x-y plane, the current function can be written as

$$I = I(X, z). \tag{3.28}$$

The tunneling current can be decomposed as a constant current in function of z - $I_0(z)$ and a small variation in function of X and z - $\Delta I(X, z)$ as the topologic dependent term so that:

$$I(X, z) = I_0(z) + \Delta I(X, z) \tag{3.29}$$

with $|\Delta I(X, z)| \ll |I_0(z)|$.

So, the variation of current related to a STM image is:

$$\delta(X) = \frac{\Delta I(X, z)}{I_0(z)}. \tag{3.30}$$

The function of tip heights $z(X)$ can be further decomposed into a constant height z_0 and the topologically dependent function $\Delta z(X)$, also the image function of STM:

$$z(X) = z_0 + \Delta z(X). \tag{3.31}$$

After substituting Eq. 3.31 into Eq. 3.29, I can be written as

$$I = I_0(z_0) + \left(\frac{dI_0(z)}{dz}\right)\Delta z(X) + \Delta I(X, z). \quad (3.32)$$

We can always choose z_0 such that $I = I_0(z_0)$. Then, we have the image function in the tunneling current:

$$\Delta z(X) = -\frac{\Delta I(X)}{\left(\frac{dI_0(z)}{dz}\right)}. \quad (3.33)$$

The STM image is determined by the variation of tunneling current. From Eq. 3.27, we know that the integration over ϵ can be decomposed out of topographic term. So, the tunneling conductance $g(r)$ is proportional to the square of modulus of transition matrix element

$$g(r) \propto |M|^2. \quad (3.34)$$

In a typical STM operation, the distance between the tip atom and the sample atom is about several Å, therefore, the Slater atomic wave functions can be used as an approximation. For a single Ti^{4+} cation, s state wave function can be written:

$$\Psi_{000}(r) \propto \frac{1}{r} e^{-\kappa r}. \quad (3.35)$$

A derivative of Eq. 3.35 generates a coefficient $\frac{\partial r}{\partial z} = \frac{\partial \sqrt{x^2 + y^2 + z^2}}{\partial z} = \cos \theta$ and a higher $\frac{1}{r^n} e^{-\kappa r}$ term. Because the r is large, we neglect this term and only keep $\frac{1}{r} e^{-\kappa r}$ term so we have:

$$\frac{\partial}{\partial z} \frac{1}{r} e^{-\kappa r} \approx \frac{-\kappa}{r} e^{-\kappa r} \cos \theta. \quad (3.36)$$

The tunneling matrix M with a d_{z^2} state tip is therefore given by Eq. 3.26

$$\begin{aligned}
M &\propto \left(\frac{3\partial^2}{2\kappa^2 \partial z^2} - \frac{1}{2} \right) \Psi_{000} \\
&= \left(\frac{3z^2}{2r^2} - \frac{1}{2} \right) e^{-\kappa r}.
\end{aligned} \tag{3.37}$$

It gives the tunneling conductance:

$$g(r) \propto |M|^2 = \left(\frac{3z^2}{2r^2} - \frac{1}{2} \right)^2 e^{-2\kappa r}. \tag{3.38}$$

For a $\text{TiO}_2(110)$ surface, we can write its total tunneling conductance $G(x, y, z)$ by summing over the lattice positions, n and m as:

$$G(x, y, z) = \sum_{n=-\infty, m=-\infty}^{\infty} g(x - na_1, y - ma_2, z) \tag{3.39}$$

with the 2D lattice constants along $[001]$ and $[110]$ as a_1 and a_2 , and the reciprocal lattice constants b_1 and b_2 . It can be expanded in Fourier series as

$$G(x, y, z) = \sum_{j, k=-\infty}^{\infty} \tilde{G}_{jk}(z) e^{i(jb_1 x + kb_2 y)} \tag{3.40}$$

and the expansion coefficient is

$$\tilde{G}_{nm} = \frac{1}{a_1 a_2} \iint e^{-i(nx + my)} g(r) dx dy. \tag{3.41}$$

The first and second non-vanishing terms of Eq. 3.40 are $\tilde{G}_{00}$, $\tilde{G}_{01}$, $\tilde{G}_{0-1}$, $\tilde{G}_{10}$ and $\tilde{G}_{-10}$ for the leading contributions by $P2mm$ symmetry of $\text{TiO}_2(110)$:

$$G(x, y, z) \approx \tilde{G}_{00} + 2\tilde{G}_{10} \cos b_1 x + 2\tilde{G}_{01} \cos b_2 y. \tag{3.42}$$

By using the following identity [36]

$$\iint dx dy r^{p-1} \cos^q \theta e^{-2\kappa + i n b_1 x + i m b_2 y} = 2\pi \left(-\frac{\partial}{2\partial \kappa} \right)^p \left(-\frac{\partial}{2\kappa \partial z} \right)^q \frac{1}{\gamma} e^{-\gamma z} \tag{3.43}$$

with $\gamma = \sqrt{(4\kappa)^2 + (nb_1)^2 + (mb_2)^2}$ and $r = \sqrt{x^2 + y^2 + z^2}$, the expansion constants can be obtained

$$\begin{aligned}\tilde{G}_{00} &= \frac{\pi}{a_1 a_2 \kappa} e^{-2\kappa z} \\ \tilde{G}_{10} = \tilde{G}_{-10} &= \left[\frac{3}{2} \left(\frac{\gamma_1}{\kappa} \right)^2 - \frac{1}{2} \right]^2 \frac{2\pi}{a_1 a_2 \gamma_1} e^{-\gamma_1 z} \\ \tilde{G}_{01} = \tilde{G}_{0-1} &= \left[\frac{3}{2} \left(\frac{\gamma_2}{\kappa} \right)^2 - \frac{1}{2} \right]^2 \frac{2\pi}{a_1 a_2 \gamma_2} e^{-\gamma_2 z}\end{aligned}\tag{3.44}$$

with $\gamma_1 = \sqrt{(4\kappa)^2 + b_1^2}$ and $\gamma_2 = \sqrt{(4\kappa)^2 + b_2^2}$.

Because $\tilde{G}_{00}$ is much larger than other terms, the total tunneling conductance is approximated as following to keep the minimal value of tunneling conductance non-negative:

$$\tilde{G}(x, y, z) \approx \tilde{G}_{00} + 4\tilde{G}_{10} \cos^2 \frac{b_1 x}{2} + 4\tilde{G}_{01} \cos^2 \frac{b_1 y}{2}.\tag{3.45}$$

For now, $\tilde{G}_{00}$ in Eq. 3.44 is treated as the constant current $I_0(z)$, and the rest part can be treated as the topographical dependent term $\Delta I(X, z)$. By Eq. 3.33, the function the STM image can be obtained:

$$\begin{aligned}\Delta z(x, y) &= \frac{16\kappa^2}{\gamma_1^3} \left[\frac{3}{2} \left(\frac{\gamma_1}{2\kappa} \right)^2 - \frac{1}{2} \right]^2 e^{-(\gamma_1 - 2\kappa)z} \cos^2 \frac{b_1 x}{2} \\ &\quad + \frac{16\kappa^2}{\gamma_2^3} \left[\frac{3}{2} \left(\frac{\gamma_2}{2\kappa} \right)^2 - \frac{1}{2} \right]^2 e^{-(\gamma_2 - 2\kappa)z} \cos^2 \frac{b_2 y}{2}.\end{aligned}\tag{3.46}$$

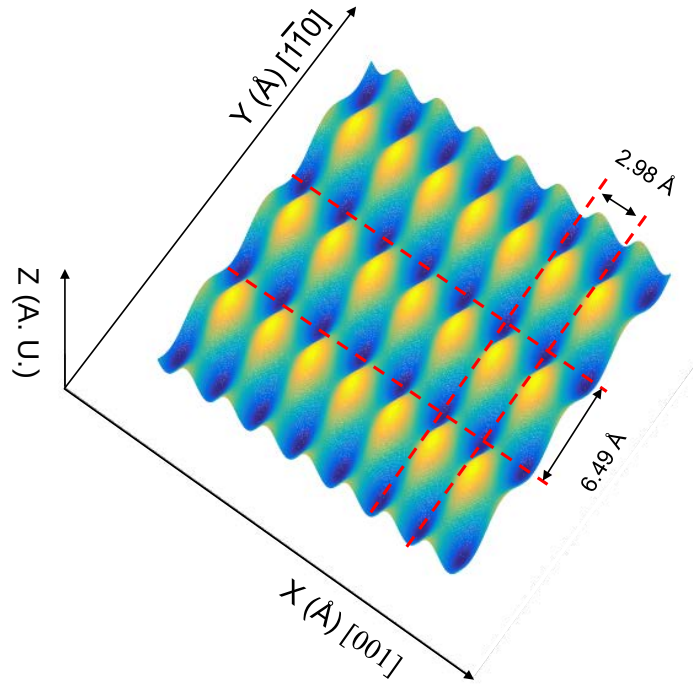


Figure 3.3 3D mapping of Eq. 3.46 with the lattice constants along [001] and [110] of $\text{TiO}_2(110)$

Fig. 3.3 shows a 3D mapping of Eq. 3.46 that Ti^{4+} cations appear as bright dots, and they space apart with each other in the lattice constants of 2D surface unit cell of $\text{TiO}_2(110)$, 6.49 Å and 2.98 Å.

3.2 Physics behind Spot Profile Analysis of LEED (SPALEED)

In LEED experiment, the incident electron beam is backscattered by the atomic lattice of the sample (See Fig. 2.15). For incident electrons with the wave length λ , the diffraction angle $\theta_{1,2}$ of an intensity maximum is obtained by the Bragg condition:

$$\theta_{1,2} = \arcsin \frac{n_{1,2}\lambda}{2a_{1,2}}. \quad (3.47)$$

And, $n_{1,2}$ denotes the beam indices corresponding to the two crystallographic directions of the surface with their lattice constants $a_{1,2}$.

Spot profile analysis of LEED (SPALEED) compares experimental data such as intensity-voltage (I-V) curves of diffraction maxima to the theoretically calculated ones from a surface model [38-42, 45]. Their agreement is estimated with a quantified reliability standard – Pendry R-factor (R_p) [41, 42]. For the conventional SPALEED, a proposed model is used to generate I-V curves. Then, the theoretical curves are compared to the experimental ones, and R_p is calculated to quantify the reliability of simulation. In contrast, the tensor LEED developed by R. J. Rous and J. B. Pendry [41], automatically varies the structure based on a reference model. By fitting the calculated curves to the experimental data, it searches a final structure which yields the lowest R_p .

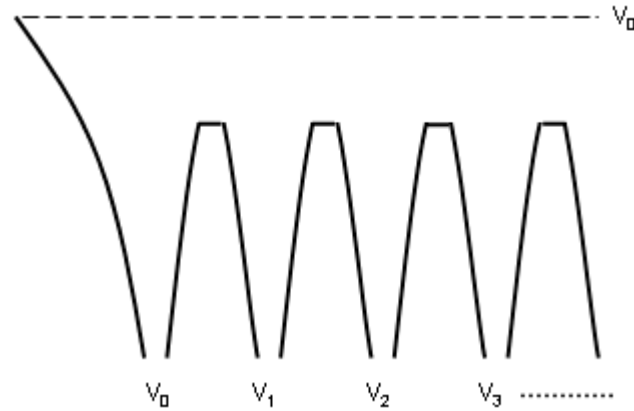


Figure 3.4 Muffin-tin potential v_i and inner potential V_0 with free space approximation in one dimension

Tensor LEED calculation models the electronic surface structure with the muffin-tin potential v_i for the i th atom in the surface and a complex inner potential V_0 with a free space approximation among v_i (An example in 1D is shown as Fig. 3.4) [40].

The total scattering potential is written as:

$$V = V_0 + \sum_i v_i . \quad (3.48)$$

We choose $|\epsilon(k_{\parallel})\rangle$ as an incident plane wave with momentum $k_{\parallel}$ parallel to the surface and k_z^+ as the perpendicular component. The diffracted state $|\Phi^+(k_{\parallel})\rangle$ can be written as the Green's function for the total scattering potential G^+ acting on the incident state $|\epsilon(k_{\parallel})\rangle$:

$$|\Phi^+(k_{\parallel})\rangle = G^+ |\epsilon(k_{\parallel})\rangle . \quad (3.49)$$

As the free space Green's function denotes G_0^+ , the total Green's function G^+ can be represented in a Born series expansion with an atomic scattering potential V :

$$G^+ = \sum_{p=0}^{\infty} G_0^+ [VG_0^+]^p . \quad (3.50)$$

By substituting Eq. 3.48 into Eq. 3.49, we can rearrange the atomic scattering matrix as

$t_i = v_i + v_i G_0^+ v_i + \dots$, so that we have

$$G^+ = G_0^+ + \sum_i G_0^+ t_i G_0^+ + \sum_{i,j;i \neq j} G_0^+ t_i G_0^+ t_j G_0^+ + \dots \quad (3.51)$$

It represents all multiple scattering paths. For example in Eq. 3.51, the first term represents the free propagation; the second term stands for the paths that electron is scattered once by any atom when summing over i ; The third terms means paths that the

electron is successively scattered by any two atoms, i and j , but no successive scatterings take place to a same atom with $i \neq j$. For a slightly varied surface, whose position of i th atom is slightly changed, the scattering potential of the i th atomic can be written as $\tilde{t}_i = t_i + \delta t_i$ with the potential change δt_i . The Green's function can be written as:

$$\tilde{G}^+ = G_0^+ + \sum_i G_0^+(t_i + \delta t_i)G_0^+ + \sum_{i,j;i \neq j} G_0^+(t_i + \delta t_i)G_0^+(t_j + \delta t_j)G_0^+ \dots \quad (3.52)$$

by rewritten in terms of δt_i , the newly assembled Green's function is

$$\tilde{G}^+ = G^+ + \sum_i G^+ \delta t_i G^+ + \sum_{i,j} G^+ \delta t_i G^+ \delta t_j G^+ \dots, \quad (3.53)$$

so Eq. 3.53 can be approximated as:

$$\tilde{G}^+ \approx G^+ + \sum_i G^+ \delta t_i G^+ + O((\delta t_i)^2). \quad (3.54)$$

Now, the Green's function of the varied surface is written in the original Green's function G^+ with the sum of contributions from the change of the scattering potential δt_i with higher order terms neglected.

To calculate the wave amplitudes $\tilde{A}_{g'}^-$ of diffracted beam with the reciprocal lattice vector g' for a varied surface ($-$ stands for outgoing direction), we project the diffraction wave in real space as a plane wave function:

$$\langle r | Z_0, k_{\parallel} \rangle = \exp(ik_{\parallel} \cdot r) \cdot \delta(z - Z_0). \quad (3.55)$$

Here, Z_0 is a user-defined vertical distance from the surface for evaluating the scattering amplitude (*e. g.* the position for measuring the intensity of diffraction maximum). The diffraction amplitude is given by Eq. 3.49:

$$\tilde{A}_{g'}^- = \langle Z_0, k_{\parallel} + g' | \tilde{G}^+ | \epsilon(k_{\parallel}) \rangle. \quad (3.56)$$

By substitution of Eq. 3.54, $\tilde{A}_{g'}^-$ can be written in terms of original amplitude $A_{g'}^-$ and the amplitude change due to the varied surface $\delta\tilde{A}_{i,g'}^-$:

$$\tilde{A}_{g'}^- = A_{g'}^- + \sum_i \delta\tilde{A}_{i,g'}^- \quad (3.57)$$

with

$$\delta\tilde{A}_{i,g'}^- = \langle Z_0, k_{\parallel} + g' | G^+ \delta t_i G^+ | \epsilon(k_{\parallel}) \rangle. \quad (3.58)$$

By Eq. 3.54, the change of diffraction amplitude $\delta\tilde{A}_{i,g'}^-$ can be written in δt_i and then expanded using the angular momentum representation

$$\delta\tilde{A}_{i,g'}^- = \sum_{l,m,l',m'} T_{i,g',l,m,l',m'} \langle r_i; l, m | \delta t_i | r_i; l', m' \rangle \quad (3.59)$$

with the expansion coefficient

$$T_{i,g',l,m,l',m'} = \langle Z_0, k_{\parallel} + g' | G^+ | r_i; l, m \rangle \cdot \langle r_i; l', m' | G^+ | \epsilon(k_{\parallel}) \rangle. \quad (3.60)$$

The total diffraction wave function can be obtained using spherical Bessel functions, j_l , and h_l , and spherical harmonics Y_{lm} from the conventional LEED calculation [40]:

$$\langle r | \Phi^+(k_{\parallel}) \rangle = \sum_{lm} A_{i;lm}(k_{\parallel}) \cdot [j_l(\kappa |r - r_i|) + t_{i,l} \cdot h_l^1(\kappa |r - r_i|)] \cdot Y_{lm}(\widehat{|r - r_i|}) \quad (3.61)$$

with

$$t_{i,l} = t_{i;lm,l'm'} = \delta_{ll'} \delta_{mm'} \frac{i}{2\kappa} [\exp(2i\delta_{i;l}) - 1]. \quad (3.62)$$

Here, $t_{i,l}$ is the atomic scattering matrix in angular momentum space as a function of phase shift $\delta_{i;l}$ and the electron wave vector $\kappa = \sqrt{2(E - V_{0r})}$ which is corrected by the surface barrier V_{0r} . Because the h_l^1 is small when $|r - r_i|$ is large, we only keep the first term of Eq. 3.61:

$$\langle r | G^+ | \epsilon(k_{\parallel}) \rangle = \sum_{lm} A_{i;lm}(k_{\parallel}) \cdot j_l(\kappa | r - r_i |) \cdot Y_{lm}(\widehat{|r - r_i|}). \quad (3.63)$$

This yields the diffraction amplitude from the reference surface for the i th atom:

$$\langle r_i; l, m | G^+ | \epsilon(k_{\parallel}) \rangle = A_{i;lm}(k_{\parallel}). \quad (3.64)$$

To obtain the second part necessary for calculating Eq. 3.60, we use the identity given by the reciprocal theorem of Green's function

$$\langle Z_0, k_{\parallel} + g' | G^+ | r_i; l, m \rangle = (-1)^m \langle r_i; l - m | G^+ | Z_0, -(k_{\parallel} + g') \rangle. \quad (3.65)$$

The wave function of a free propagating electron with the normalization factor as a function of the reference surface unit cell area Ω is therefore

$$\begin{aligned} \langle r | G_0^+ | Z_0, -(k_{\parallel} + g') \rangle &= \frac{1}{2i\kappa k_{g'z}^+ \Omega} \cdot \exp[ik_{g'}^+ \cdot (r - Z_0)] \\ &= \frac{1}{2i\kappa k_{g'z}^+ \Omega} \cdot \langle r | G_0^+ | \epsilon(-(k_{\parallel} + g')) \rangle. \end{aligned} \quad (3.66).$$

where $k_{g'}^+ = (k_z^+, k_{\parallel} + g')$ is the incident beam vector plus the reciprocal lattice vector g'

and $k_{gz}^+ = \sqrt{2E - |k_{\parallel} + g'|^2}$. The result can be written by keeping the first term in Eq. 3.53:

$$\langle Z_0, k_{\parallel} + g' | G^+ | r_i; l, m \rangle = \frac{1}{2i\kappa k_{g'z}^+ \Omega} \cdot A_{i;lm}(-(k_{\parallel} + g')). \quad (3.67)$$

The tensor is now written as the result of a conventional LEED calculation

$$T_{i,g',l,m,l'm'} = \frac{1}{2i\kappa k_{g'z}^+ \Omega} (-1)^m \cdot A_{i;lm}(-(k_{\square} + g)) \cdot A_{i;l'm'}(k_{\square}). \quad (3.68)$$

With Eq. 3.59 and 3.60, we can calculate the amplitude change contributed by the scattering potential change δt_i .

In order to optimize the surface structure, the change of the amplitude δt_i must be written as a function of atomic displacement δr_i . The linear tensor LEED approximation [41] is used for this purpose. By using the finite translation operator with setting $\hbar=1$, the change in amplitude δt_i in a linear momentum representation can be rewritten in the atomic displacement δr_i :

$$\langle k' | \delta t_i | k \rangle = \langle k' | t_i | k \rangle (\exp(i[k' - k] \cdot \delta r_i) - 1). \quad (3.69)$$

If the displacement is much smaller than the electron wave length that $\kappa |\delta r_i| \ll 1$ ($\kappa = \sqrt{2(E - V_{0r})}$), the approximation of Eq 3.69 can be made by using the infinitesimal translator:

$$\langle k' | \delta t_i | k \rangle \approx \langle k' | t_i | k \rangle (i[k' - k] \cdot \delta r_i). \quad (3.70)$$

In this approximation, δr_i in an angular momentum basis can be rewritten as:

$$\begin{aligned} \langle r_i; l'' m'' | \delta t_i | l m; r_i \rangle = \sum_{l' m'} \int \langle r_i; l'' m'' | k' \rangle \langle k' | t_i | r_i; l' m' \rangle \langle r_i; l' m' | k \rangle \\ \langle k | r_i; l m \rangle i(k' - k) \cdot \delta r_i d\Omega_k d\Omega_{k'}. \end{aligned} \quad (3.71)$$

We note that $k \cdot \delta r_i$ is a scalar product which can be rewritten in the form of spherical harmonics Y_{lm} . The product of z component is $K^z \delta r_i^z = \delta r_i^z |K| \cos \theta = \delta r_i^z |K| Y_{10}$ and the products of the other components can be similarly treated. Then, using the Gaunt coefficient $C_{lm, l'm', l''m''} = \int Y_{lm}(\Omega) Y_{l'm'}(\Omega) Y_{l''m''}(\Omega) d\Omega$ and the orthogonality of Y_{lm} , Eq. 3.71 can be written as:

$$\langle r_i; l'' m'' | \delta t_i | l m; r_i \rangle = \alpha_{i, l, m, l', m'} \cdot \delta r_i \quad (3.72)$$

where the vector $\alpha_{i, l, m, l', m'}$ has Cartesian components:

$$\begin{aligned}
\alpha_{i,l,m,l',m'}^x &= (-1)^{m'} i \sqrt{4\pi/3} \kappa(t_{i;l} - t_{i;l'}) C_{lm,10,l'm'} \\
\alpha_{i,l,m,l',m'}^y &= (-1)^{m'} i \sqrt{4\pi/3} \kappa(t_{i;l} - t_{i;l'}) (C_{lm,11,l'm'} + C_{lm,1-1,l'm'}) \\
\alpha_{i,l,m,l',m'}^z &= (-1)^{m'} i \sqrt{4\pi/3} \kappa(t_{i;l} - t_{i;l'}) (C_{lm,11,l'm'} - C_{lm,1-1,l'm'}).
\end{aligned}$$

The change of spectral amplitude $\delta \tilde{A}_{i,g'}^-$ can be expressed in a function of atomic displacement δr_i for now:

$$\delta \tilde{A}_{i,g'}^- = \sum_{l,m,l',m'} T_{i,g',l,m,l',m'} \alpha_{i,l,m,l',m'} \cdot \delta r_i. \quad (3.73)$$

Summing over the i th atom in the entire angular moment space can give a total change of intensity $\delta A_{g'}$ for the diffracted beam g' and we have the original amplitude A_g^- from the conventional calculation. Therefore, the total intensity of diffracted beam g' for the varied surface is

$$I_{g'} = \frac{|k_{g'z}^-|}{|k_z^+|} |A_g^- \delta_{gg'} + \delta A_{g'}|^2. \quad (3.74)$$

To estimate a quantitative agreement between the theoretic and experimental spectra, the Pendry R_p is developed as a function of the derivative of beam intensity $L_{e/t} = I_{e/t}' / I_{e/t}$ (e for experimental and t for theoretical) [41, 42]. $L_{e/t}$ is further transformed into a Lorentz like spectra $Y_{e/t} = \frac{L_{e/t}}{(1 + V_{oi}^2 L_{e/t}^2)}$. The Lorentz-like spectra emphasize the contribution from peak positions, which is more sensitive to structure, but not peak heights [41, 42]. R_p is therefore given as a ratio of the integrations over the beam energy from E_1 to E_2 , between a squared difference and a squared sum of the spectra

$$R_p = \frac{\int_{E_1}^{E_2} (Y_e - Y_t)^2 dE}{\int_{E_1}^{E_2} (Y_e + Y_t)^2 dE}. \quad (3.75)$$

Its value varies from the smallest value 0, suggesting a perfect match, and the maximal value 2, suggesting a total mismatch.

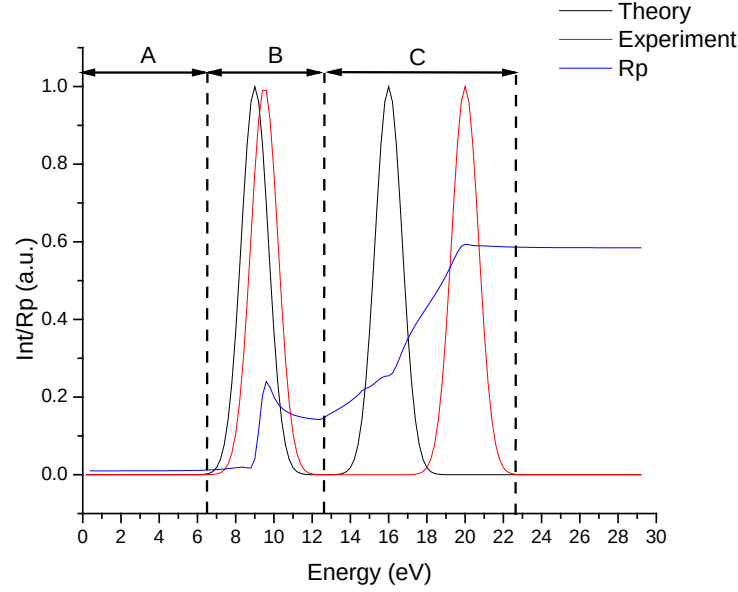


Figure 3.5 Pendry R-factor and experiment/ theory I-V curves

To explain R_p , two hypothetical I-V curves for theory and experiment are shown in Fig. 3.5. Two theoretical peaks are centered on 9 eV and 16 eV (Black curve), and two experimental ones are placed at 10 eV and 20 eV (Red curve). The value of R_p is plotted as a blue curve from 0 eV to 30 eV. In the phase A (0 eV to 6 eV), the R_p remains zero because the IV curves perfectly match. In the beginning of the phase B (6 eV to 9 eV), the R_p grows slowly because the similar derivatives of the experimental and theoretical curves in the function $L_{e/t}$, and they merely contribute to R_p . In the later part of phase B, the R_p value quickly rises to 0.22 as a result of 1 eV difference between the peak positions. It then

slowly drops back to 0.17 due to the average effect for the integration from 10 eV to 13 eV. Such R_p value of 0.17 suggests an acceptable agreement between two curves. In the phase C (13 eV to 23 eV), the R_p value steeply rises to 0.6 due to the totally mismatch peaks centered at 16 eV and 20 eV. As one can see in the figure, the mismatched positions of the peaks dramatically worsen the R_p value pointing a poor agreement between experimental and theoretical spectra.

Eq. 3.73, Eq. 3.74 and Eq. 3.75 can be used to obtain $R_p(\delta(r_i))$ as a function of i th atomic displacement δr_i for a varied structure, so that the structural optimization to achieve the minimal R_p is possible. To optimize the structure, the algorithm of direction-set method [46] is used to generate a set of different search directions in the surface of $R_p - \delta r_i$, and finds the fastest direction to decrease R_p within a pre-set distance. The search directions are iteratively updated to further lower the R_p until it reaches the minimal position, which satisfies a convergence test. Such an algorithm has an advantage of using computation resource economically without finding the reciprocal function of $R_p(\delta(r_i))$. However, it doesn't ensure finding the globally minimum in the space of δr_i . Another search algorithm is needed to avoid such local minimum trapping, and it will be discussed in CHAPTER FOUR.

The simulation package, Symmetrized automated tensor LEED (SATLEED) [39], is written to realize above calculations and algorithm. The program is divided into two parts: TLEED1 and TLEED2. As Fig. 3.5 shows, TLEED1 requires an input of a

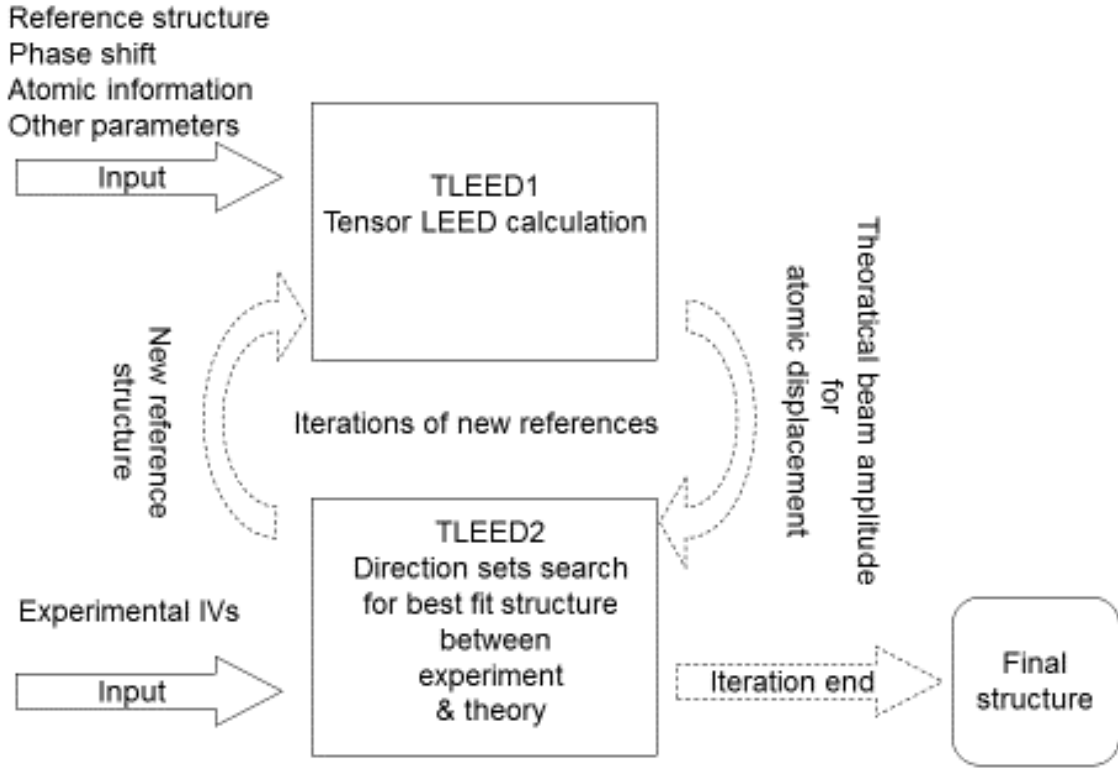


Figure 3.6 Flow diagram for SATLEED

reference structure (usually proposed from bulk structure), the atomic phase shifts $\delta_{i,l}$ (calculated from other programs), and other information like temperature and atomic mass. The TLEED1 calculates and stores the matrices of Eq. 3.72 using the reference structure.

TLEED2 takes the experimental I-V curves as inputs for the comparison to the calculated I-V spectra. It also varies δr_i by the direction set method to minimize R_p , and generates the optimized atomic displacements. The resultant structure, which includes these displacements, can be used as a new reference to be iteratively calculated and optimized in TLEED1 and TLEED2. Once the calculation converges to itself in the iteration, the final

optimized structure is obtained. The further details in performing SATLEED simulation will be discussed in the next chapter.

CHAPTER FOUR

Result and Discussion

4.1 SPALEED Structure Determination of (1x1) TiO₂(110) Relaxation

In this work, (1x1) TiO₂(110) surface structure is first investigated using the SPALEED analysis and will be used as a reference for the subsequent study of the (1x2) reconstructed TiO₂(110). The experimental LEED I-V spectra recorded at temperature 140 K [11] are used as an input along with the bulk structure for the SATLEED program. By an iterative process, the program calculates the structure best fit to the experiment data. The final structure can be reached with a user-specified criterion, typically given as the R-factor (R_p). If the value of R_p is less than 0.3, the result is generally considered credible for a metal oxide surface. In the range of 0.3~0.5, the R_p merely implies that an indefinite correlation exists between the experimental data and the structure. A R_p higher than 0.6 indicates no correlation between the calculated structure and the experimental data.

In order to calculate the theoretical intensity of scattered electron waves, phase shift information of the electron waves from the atomic scattering potential must be obtained. The phase shifts of titanium and oxygen (Fig. 4.1) are generated using the Barberi/Van Hove package [38, 39]. They are calculated using a partial-wave expansion method of angular momentum L as a function of incident beam energy (55-326 eV). The

results show that the expansion up to $L = 8$ is sufficient for both Ti and O as the contributions from higher L terms become negligible.

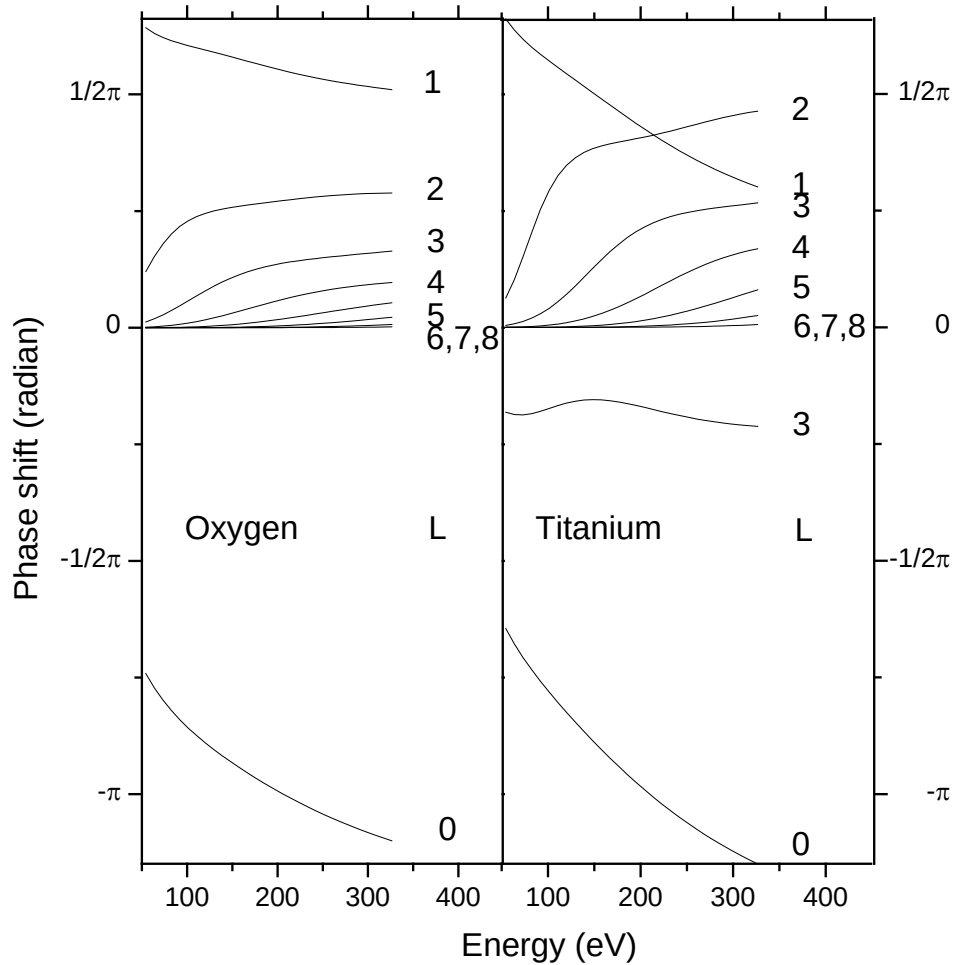


Figure 4.1 Phase shift of (1x1) $\text{TiO}_2(110)$ for oxygen and titanium

A model of (1x1) $\text{TiO}_2(110)$ for the initial reference structure is shown in Fig. 4.2. It contains 25 atoms with the top bridging oxygen labeled as the atom #1 on surface [2]. The position of Z direction is defined as the inward normal toward bulk along $[\bar{1}\bar{1}0]$. The X and Y axes are aligned along $[\bar{1}10]$ and $[001]$ following the convention of the program

[38]. (1x1) $\text{TiO}_2(110)$ 2D unit cell has the $P2mm$ symmetry. In the spatial search, 25 independent degrees of freedoms for 21 inequivalent atoms are optimized. In order to prevent unphysically overlapping of the scattering potential between the two elements, the separation ratio of Muffin-tin radius is set as 0.5. The imaginary part of the inner potential V_{oi} is set as -5.0 eV to take into account for the attenuation and the broadening of electron scattering peak due to inelastic scattering [39].

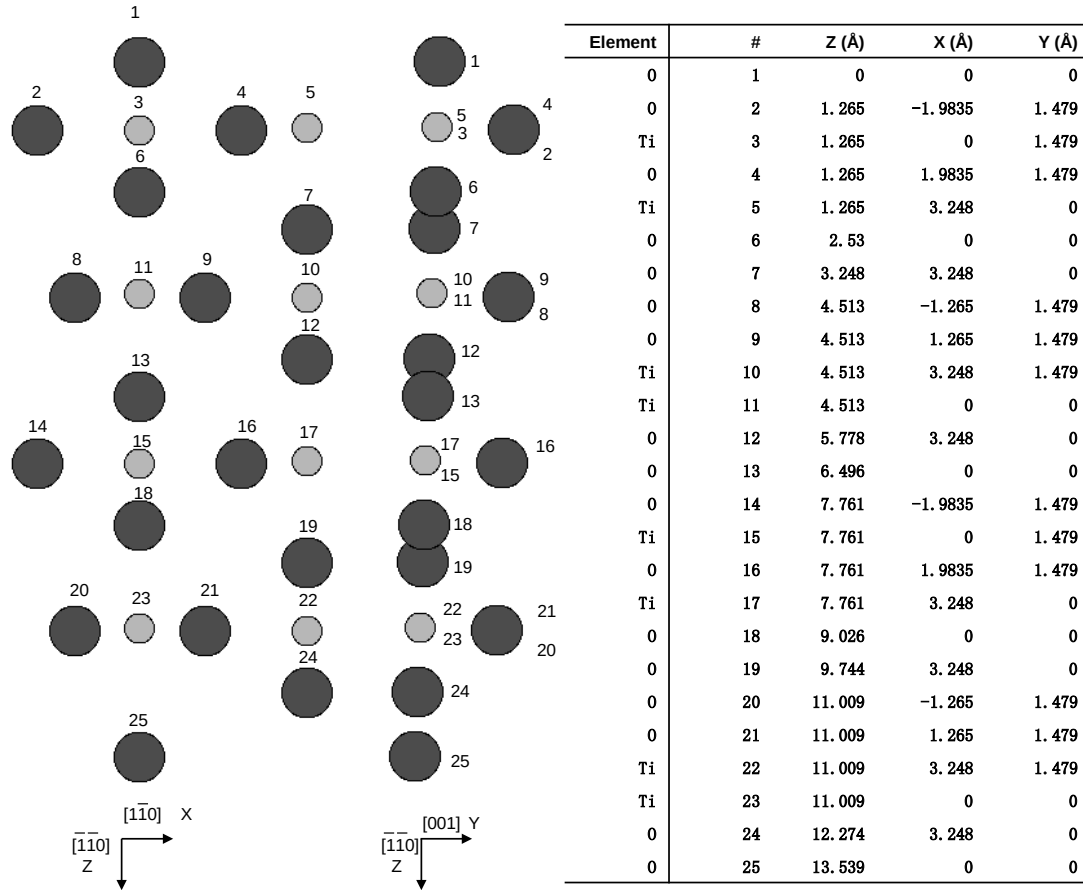


Figure 4.2 Reference structure input of $\text{TiO}_2(110)$ (Left: bulk structure; big sphere- oxygen; small sphere- titanium; right: atomic information and coordinates)

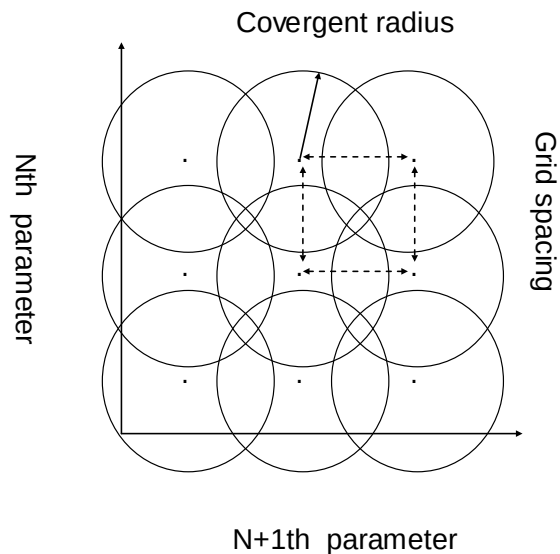


Figure 4.3 Grid search in parameter space and convergence coverage

A bash script [47] is written to vary the 25 atomic coordinates from the initial position of the algorithm (Appx. A). The script generates a grid of search initiation (Fig. 4.3, dot grid) and submits jobs to a Baylor cluster computer. The grid spacing (dashed arrow) is $0.15 \text{ \AA}$ in each atomic displacement, and the convergent radius (solid arrow) of the algorithm is $0.5 \text{ \AA}$. The convergent spheres (circles in the Fig. 4.3) cover the region around each grid point in the entire parameter space. The direction set algorithm generates a R_p value corresponding to the local minimum in the region near each grid point. By selecting the result of the lowest R_p in all these regions, the global minimum can be obtained, and the local minimum trapping caused by direction set method can be avoid.

After the optimized structure is determined, the other consideration such as isotropic vibration, to which LEED is sensitive, needs to be examined for the final refinement. In SATLEED, it is parameterized as a function of Debye temperature [38, 40]. Its mean square of amplitude is given by

$$\langle u^2 \rangle = \frac{9\hbar^2 T}{mk_B \Theta_D} \quad (4.1),$$

in which m , k_B , T and Θ_D denote the atomic mass, Boltzmann constant, Temperature and Debye temperature respectively. In Debye model, Θ_D only depends on the phonon density of the crystal. So for a compound like TiO_2 , Θ_D can be given as a single value in either theory or experiment. However, the vibrational amplitudes for Ti and O are different due to their different masses. Also due to the broken symmetry at the crystal surface, the thermal vibrational modes of the surface atoms may be different from that of bulk atoms [48-52]. As a simplified model, two Debye temperatures, one for the surface atoms #1 through #5 and the other for the rest, are independently searched within the limitation of SATLEED and computational efficiency. The search result yields that the optimized Debye temperature is 300 K for the surface atoms and 450K for the rest atoms. It indicates that vibration of surface atom is larger than that of bulk, which is consistent with other reports [50-52].

The theoretical I-V curves from the final structure are compared to those experimental curves in Fig 4.4. The SATLEED input files for the final structure are also

listed in Appx. B. Overall, the final result yields the average value of R_p as 0.29. It is particularly convincing with the value of energy range per degree of spatial search

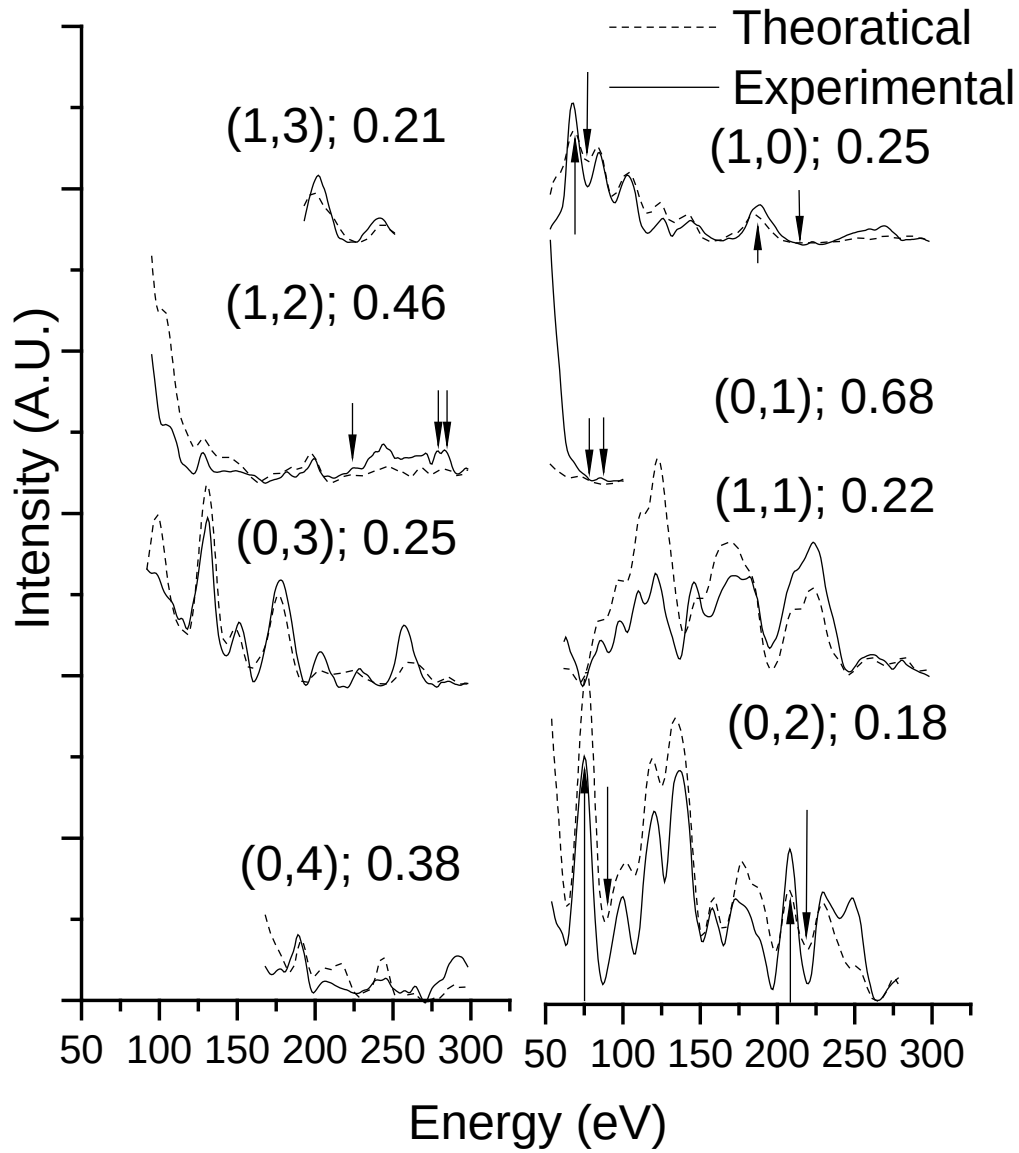


Figure 4.4 Comparison between theoretical and experimental I-V curves and the R_p

freedom, 65 eV, for exceeding the minimal acceptable standard, 30 eV [38 - 40]. Such energy range is given by the total energy range of 1370 eV for all the experimental

spectra divided by the 21 degrees of freedom used in analysis. The purpose is to avoid the possibility that excessive degrees of spatial search freedom are used to create unnecessary peaks in calculated curves for best-fitting the experimental spectra [38 - 40].

Specifically, the calculated positions of major peaks from various beams match well with the experimental ones. The calculated (0,2) beam has the lowest R_p value of 0.18. In Fig 4.4, the upward arrows mark maximum positions of the (0, 2) beam at 75 eV and 209 eV, respectively. Similarly, minima at 92 eV and 220 eV are pointed out by downward arrows. All their positions show good match, only at most 3 eV deviation either on low or high energy side of the spectrum. Most of the other beams also yields low R_p values, for example, 0.25 for (1,0) beam, 0.21 for (1,3), and *etc.* On the low energy side of (1,0) beam, the experimental maximum at 63 eV matches with the theoretical one well. Next to this maximum, the position of minimum at 70 eV matches with the experimental one as well. On the high energy side, the experimental maximum at 181 eV slightly deviates from the theoretical one for a difference less than 5 eV. In the following energy range, the positions of experimental and theoretical minima near 224 eV overlap together as well.

While the peak positions are in good agreement for the beams with low R_p values (*e. g.* (1,3), (0,3) (0,1), (1,0) and (1,1)), peak heights are more discrepant. One of the reasons may be attributed to inaccurate accounting of background intensity. The experimental spectra suffer from inelastically scattered electrons contributing to the

background. The diffracted beam intensity may decay faster in higher energy than expected since the surface can be damaged by electrons with higher energy. On the other hand, the flux of incident beam increases with higher electron energy, so does the background intensity. The contrast between the beam and the background may become weak, resulting in inaccurate estimates of intensity. For the beams with higher R_p values such as (1,2) and (0,1) ($R_p = 0.46$ & 0.68), unmatched peak positions are marked by arrows in Fig. 4.4. For the beam (1,2), the experimental peak at 220 eV is not shown in the theoretical one. At 281 eV where a double peaks are observed experimentally, there is only a single peak in theoretical curve. Similarly for the beam (0,1) with the highest value of R_p 0.68, the experimental minimum and maximum indicated by arrows are not replicated in the calculated curve. These unmatched peak positions contribute to the larger R_p values as we illustrated in CHAPTER THREE.

The optimized structure is shown in Fig. 4.5, and the relative displacements from the bulk positions are also listed in Table 4.1. In order to visualize the related displacements, the optimized structure is overlapped with the bulk structure aligning at the positions of the atom #25 (Fig. 4.5), below which the rest structure is fixed as bulk.

The surface relaxation features have been compared with other reports by LEED and SXRD analyses in Table 4.2 [11, 12]. Both Fig. 4.5 and Table 4.2 clearly show that the bridging Ti-O bond between atom #1 and #3 is contracted to 1.852 Å. The amount of the contraction is identical to that from the other LEED report, but the study using SXRD

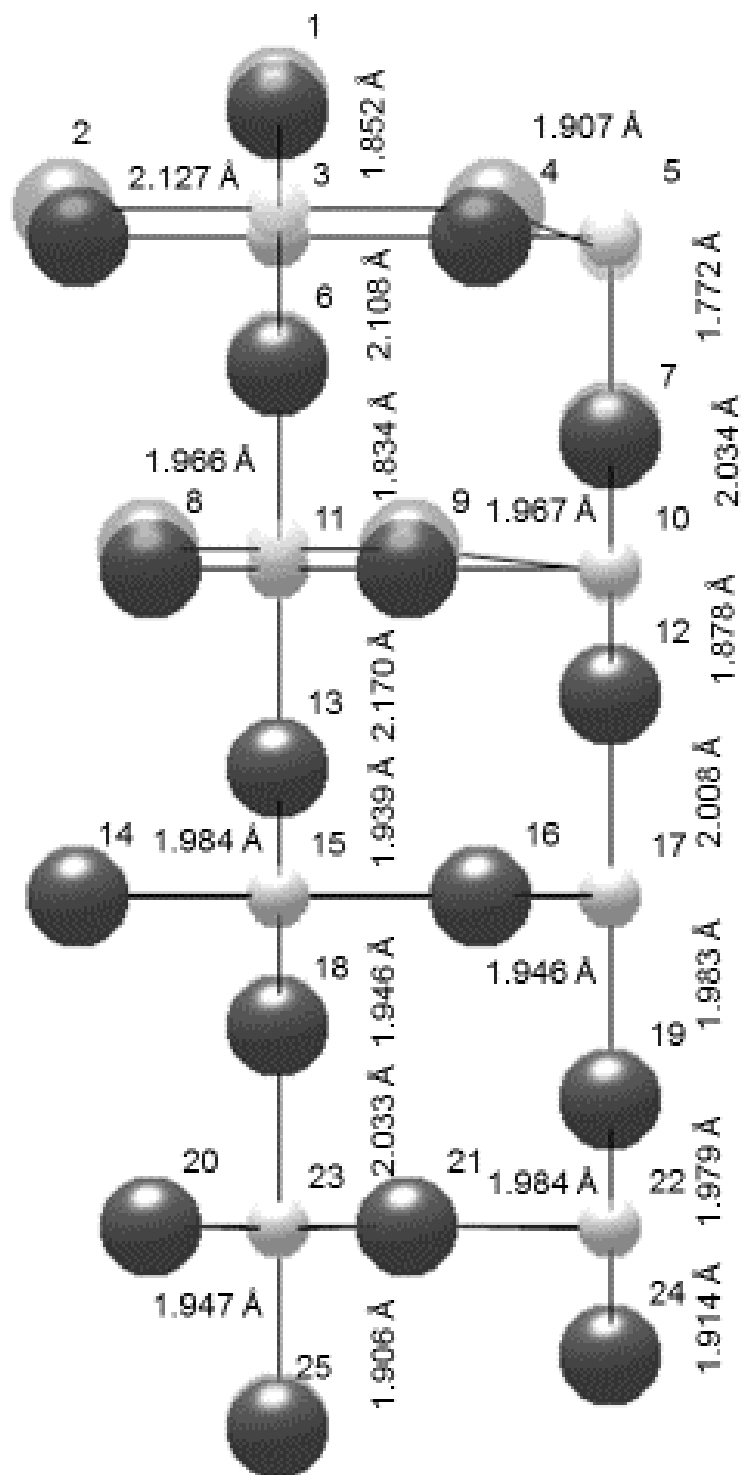


Figure 4.5 Atom displacements and bond distances in optimized structure (Large dark sphere: bulk oxygen; small dark sphere: bulk titanium; large light sphere: relaxed oxygen; small light sphere: relaxed titanium)

Table 4.1 Atom displacements of (1x1) TiO₂(110) relaxation

Element	#	ΔZ (Å)	ΔX (Å)
O	1	-0.092	0
O	2	-0.214	-0.0931
Ti	3	-0.241	0
O	4	-0.214	0.0931
Ti	5	0.182	0
O	6	-0.012	0
O	7	0.008	0
O	8	-0.110	0.0323
O	9	-0.110	-0.0323
Ti	10	0.127	0
Ti	11	-0.153	0
O	12	0.003	0
O	13	0.015	0
O	14	0.046	-0.1167
Ti	15	-0.045	0
O	16	0.046	0.1167
Ti	17	0.102	0
O	18	0.111	0
O	19	0.043	0
O	20	-0.011	-0.1055
O	21	-0.011	0.1055
Ti	22	0.058	0
Ti	23	-0.059	0
O	24	0.111	0
O	25	0.020	0

reports a larger contraction to result in a shorter bond length of 1.718 Å. The Ti-O bond between atom #3 and #6 is stretched to 2.108 Å. This elongated bond distance is close to 2.075 Å, but somewhat larger than 1.992 Å, which are reported by Ref. 11 and 12,

respectively. The 5-fold coordinated Ti (atom #5) is sagged toward bulk by 0.182 Å, 0.19 Å and 0.16 Å, respectively, in the three works.

Table 4.2 Comparison of relaxation features among different reports and bulk structure

Relaxation Features	This work	LEED [11]	SXRD [12]	Bulk
Bridging bond (#1-3)	1.852 Å	1.852 Å	1.718 Å	1.946 Å
Sub-surface Ti-O bond (#3-6)	2.108 Å	2.075 Å	1.992 Å	1.946 Å
5-fold coordinated Ti sagging dist. (#5)	0.182 Å	0.190 Å	0.160 Å	0 Å

The agreement between two LEED analyses, this work versus Ref. 11 are within 0.03 Å. The high precision agreement results from sharing the same experimental data reported by R. Lindsay *et. al.* [11]. Small differences in final structures are in part due to the fact that the optimizable layers are four slab layers in this work whereas two slab layers are used in Ref. 11. In the modeling of both works, the atoms below the optimizable layers have been fixed as bulk. However, these atoms are physically relaxed as a result of the fact that, the level of the relaxation is strongest on the surface and is diminishing when the depth of relaxed atoms goes higher. Thus, their relaxations physically occur and experimentally contribute to the LEED spectra. And, the program cannot optimize their positions to simulate the physical relaxation when best fitting the experimental data. It causes an issue that, in order to mimic their contributions, the program may over-drive the

atomic displacements in optimizable layers, and yield a deviated final structure. This issue can be lessened when more and deeper optimizable layers are modeled so that the depth of bulk-fixed atoms below them becomes higher as well. Because of the attenuation of incident electrons, their experimental contributions can be limited to a negligible level. Therefore in this work, the final structure modeled with more optimizable layers is less deviated from the physical one by the simulation program than that in Ref. 11.

Generally, the relaxation of the sub-surface layers here can be understood as a consequence from the structural compensation due to the missing atoms. The terminated surface creates the severed Ti-O bonds (Dangling bonds) on bridging oxygen and 5-fold coordinated Ti (atom #1, 5 respectively). To compensate the missing titanium above the bridging O, the whole octahedra (atom #1, 3, 4 and 6) centered at 6-fold coordinated Ti is pulled upward. The atom #1, 2 or 4, and 3 move upward by about 0.1 Å, 0.2 Å and 0.2 Å, respectively whereas the atom #6 rises only by 0.01 Å. To compensate the missing O on 5-fold coordinated Ti site (atom #5), all the surrounded O atoms (#2 or 4 and 7) are pulled closer. The bond between atom #4 and 5 is shortened to 1.907 Å from the bulk value of 1.947 Å. The bond between atom #5 and 7 is compressed to 1.772 Å. Also for compensating the missing oxygen, the 5-fold coordinated Ti is attracted to a lower position for bulk containing more oxygen.

The relaxation below these atoms exhibits a similar structural trend. Such structure can be regarded as a transition from the relaxed surface to bulk. The atoms of #8,

9 and 11 are pulled upward (~ 0.15 Å) to follow the elevation of the octahedron including atom #1, 3, 4 and 6. The Ti # 10 is moved lower for 0.13 Å similar to the sagged downward 5-fold coordinated Ti #5. Comparing with the displacement of the two titanium atoms on the surface (Ti #3 and #5, displacement ~ 0.2 Å), the downward movements of Ti #10 and 11 are significant smaller (displacement < 0.15 Å). The bond between O #9 and Ti # 10 is similarly bent toward 5-fold coordinated Ti like the Ti-O bond (atom #4 to 5). It is also less shortened to 1.967 Å from bulk value 1.983 Å. Besides these atoms, the rest of the atoms below (atom #12 through 25) is basically bulk-like as shown in Fig. 4.5.

Other than these relaxation features, the changes of bond lengths also reveal a consistent pattern of contraction-elongation sequence along chains of Ti-O bonds running towards bulk. Those bonds connecting to the surface atoms (atom #1 to #3 and atom #5 to #7) are all compressed (1.862 Å and 1.772 Å, respectively). Their subsequent Ti-O bonds toward bulk (atom #3 to 6 and #7 to 10) are elongated to 2.108 Å and 2.034 Å. Below these bonding layers, similar sequences repeat along $[\bar{1}10]$. In the bond chains of atom #6 to 11 to 13 and #10 to 12 to 17, the distances of bonds are contracted, and then elongated as 1.834 Å – 2.170 Å and 1.878 Å – 2.008 Å. In deeper layers, the bond lengths converge to the bulk values. For example, the bonds lengths in atomic chain #13 to 15 to 18 are 1.939 Å and 1.946 Å (bulk value 1.946 Å). And in atomic chain #17 to 19 to 22, they are 1.983 Å and 1.979 Å (bulk value 1.983 Å).

Such bond patterns can also be understood as an electrostatic interaction. Along $[1\bar{1}0]$, the 2-fold coordinated oxygen on the surface, whose bonded Ti cation is missing, strongly attracts the chains of Ti cations (Ti #3, 11, 15, and 23). And, the Ti chain (Ti #5, 10, 17 and 22) is attracted downward by the bulk with more oxygen. Meanwhile, the oxygen atoms connecting Ti chains displaced less along $[\bar{1}\bar{1}0]$. As Table 4.1 shows, the Ti atoms of #3, 11 and 15 move upward by 0.24 Å, 0.15 Å and 0.05 Å, respectively, with an average displacement of 0.14 Å. The oxygen atoms in this Ti chain along $[\bar{1}\bar{1}0]$ (O #6, 13 and 18) only move for -0.01 Å, 0.02 Å and 0.11 Å. The average displacement is 0.04 Å, which is much less than that of Ti atoms. Similarly in Ti chain of atom #5, 10 and 17, the downward displacements are 0.18 Å, 0.13 Å and 0.10 Å with an average value of 0.14 Å. The oxygen chain between them (O # 7, 12 and 19) have vertical displacements of 0.01 Å, 0.00 Å and 0.04 Å with a significant smaller averaged value of 0.02 Å. Therefore, the relaxation can be viewed as Ti atoms displaced in the relatively stationary O octahedral cages resulting the alternating sequence of the contracted-elongated bonds.

4.2 SPALEED Structure Determination of (1x2) TiO₂(110) Reconstruction

To calculate LEED I-V curves of (1x2) TiO₂ surface modeled by Ti₂O added row, the phase shifts of scattered waves from atomic scattering potential need to be obtained first. Because LEED optics used in this work provides more experiment data for the low energy spectra, the optimized muffin-tin potential method, which yield an improved

accuracy in low energy scattering [49], is used to calculate phase shifts. The phase shifts for titanium and oxygen are plotted in Fig. 4.6. As discussed in the (1x1) $\text{TiO}_2(110)$ calculation, the phase shifts with expansion terms of L up to 8 are sufficient for the calculation. The phase shifts are tested through calculating the final structure of (1x1) TiO_2 ($R_p = 0.29$). The best-fitting yields a similar R_p value of 0.31 without any

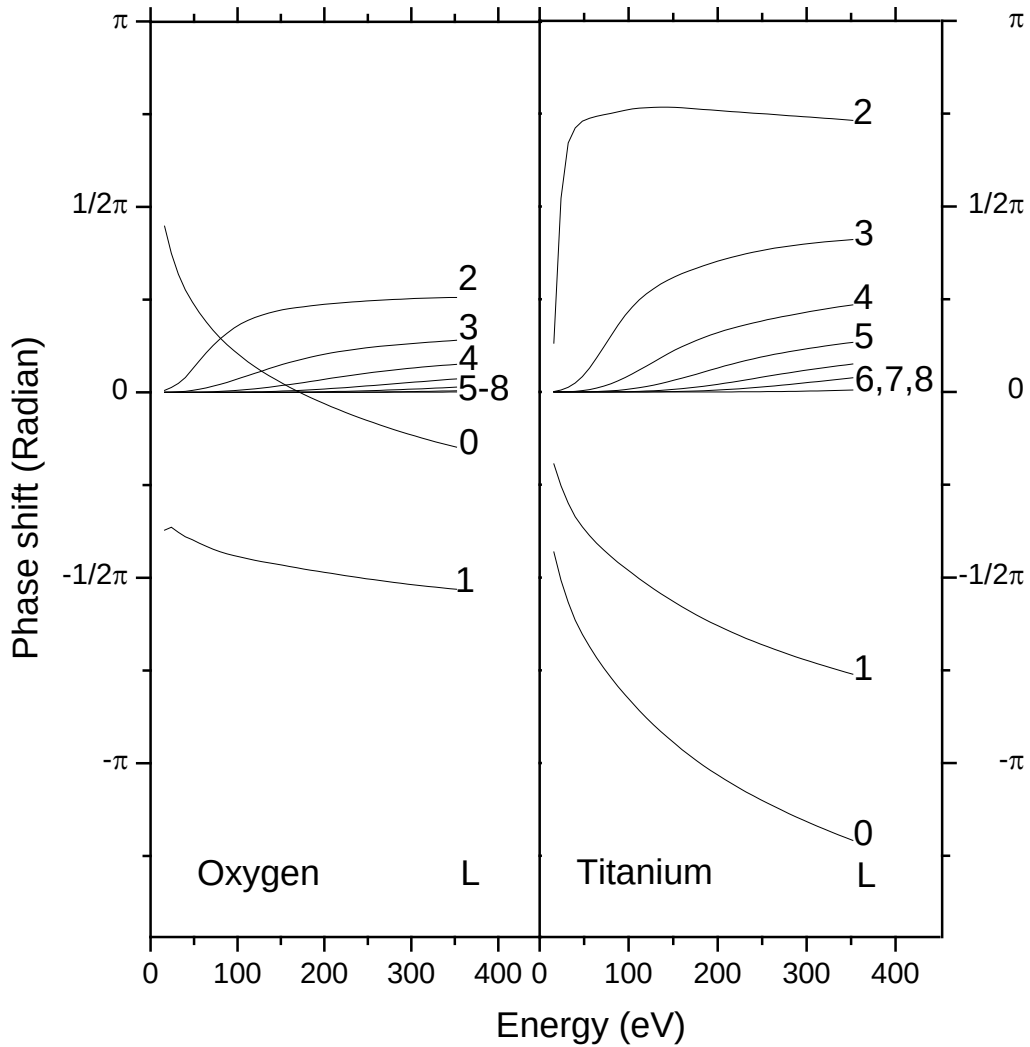


Figure 4.6 Phase shifts of (1x2) $\text{TiO}_2(110)$ for oxygen and titanium

refinement, and the optimized structure barely changes from the previous converged structure. The good agreement between the two methods suggests the phase shifts from optimized muffin-tin potential can provide consistent scattering information.

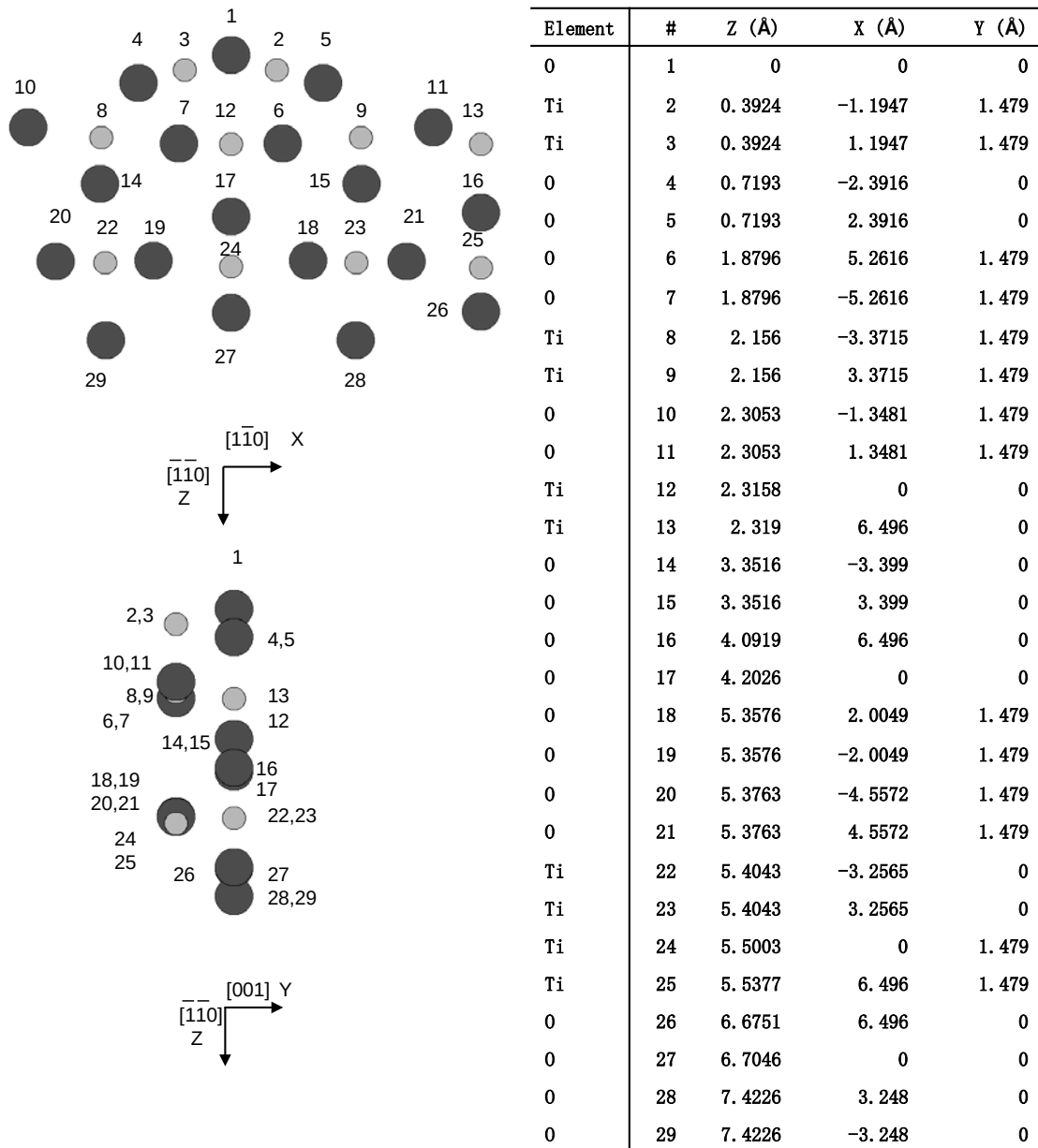


Figure 4.7 Reference structure input of (1x2) TiO₂(110) reconstruction as the first 29 atoms in Ti₂O added row model and the atomic information (Left: bulk structure; big sphere - oxygen; small sphere - titanium; right: atomic number and coordinates)

In the previous analysis of (1x1) TiO₂ (Sec. 4.1), atoms in the fourth slab layer are found to relax with a displacement of 0.05 Å. For the (1x2) reconstructed surface modeled with Ti₂O or Ti₂O₃ added row, we define the number of slab layer by counting the slab layer of its underlying TiO₂ units (see Sec. 1.2). Two optimizable slab layers are used in this work due to the limitation in computational resources. Thus, the model of the first 29 atoms in a DFT calculated structure for (1x2) Ti₂O added row [13] is utilized as the initial structure (Fig. 4.7). The coordinate system of the reference model is set as the same as CH 4.1 and is shown in Fig 4.7. In the spatial search of the *P2mm* symmetry for the 2D unit cell of the (1x2) reconstruction, 29 independent degrees of freedom for the 29 inequivalent atoms are optimized. Below the atom #29, the structure is fixed to be bulk of rutile TiO₂(110). The inner potential $V_{\text{O}i}$ [40] is set as -5.0 eV as the same as in the Ref. 18. The total energy range for the LEED I-V curves is 1360 eV and the energy range per spatial search freedom is 47 eV, which is larger than the minimal standard, 30 eV [38-40]. All the other parameters and search scripts are kept the same as in Sec. 4.1.

The low temperature (LT) LEED experiment is known to provide sharper diffraction pattern for incident electrons of higher energy. For the incident electrons of higher energy with a longer attenuation length, the multiple scattering is more likely to occurs that the electrons are successively scattered by many atoms. The thermal vibration of these atom is incoherent [40]. The path of electrons varies after each time they are scattered by every atom positioned at off-equilibrium. As a consequence for the case with

a higher temperature, multiply scattered electrons travel in a larger number of distributed paths and cause decoherence in a diffraction beam. To obtain sharper diffraction spots, the experiment is performed at LT ($T = 190$ K). Only those fractional and integer beams that exhibit clean intensity contrasts are chosen for the LEED I-V analysis.

It is well-known that (1×1) and (1×2) reconstructed surface can co-exist within a LEED sampling area [53]. For a surface with mixed (1×1) and (1×2) domains in LEED experiment, both domains contribute to the integer spots of diffraction maxima, but only (1×2) domain can contribute to the fractional spots. To exclude the possible contribution from (1×1) domain, integer spots are not used in LEED calculation, only the I-V curves from the fractional spots of best contrast are used for studying (1×2) structure, and the $(1.5, 1)$ spot is such an example.

To evaluate the data qualities, the I-V curve of $(1.5, 1)$ spot is compared with that reported in Ref. 18 and they are plotted in Fig. 4.8 (Black lines and dashed blue, respectively). The comparison shows good agreement in peak positions with those reported, for example, the positions of intensity maxima at 68 eV, 112 eV, 129 eV, 142 eV and 153 eV. Also, this I-V curve has been analyzed by the peak fitting function using Origin Lab for checking the consistency of peak width. It shows that the full width at half maximum (FWHM) ranges from 7 to 15 eV, and the values agree well with those reported in literature (7-30 eV) [38, 40].

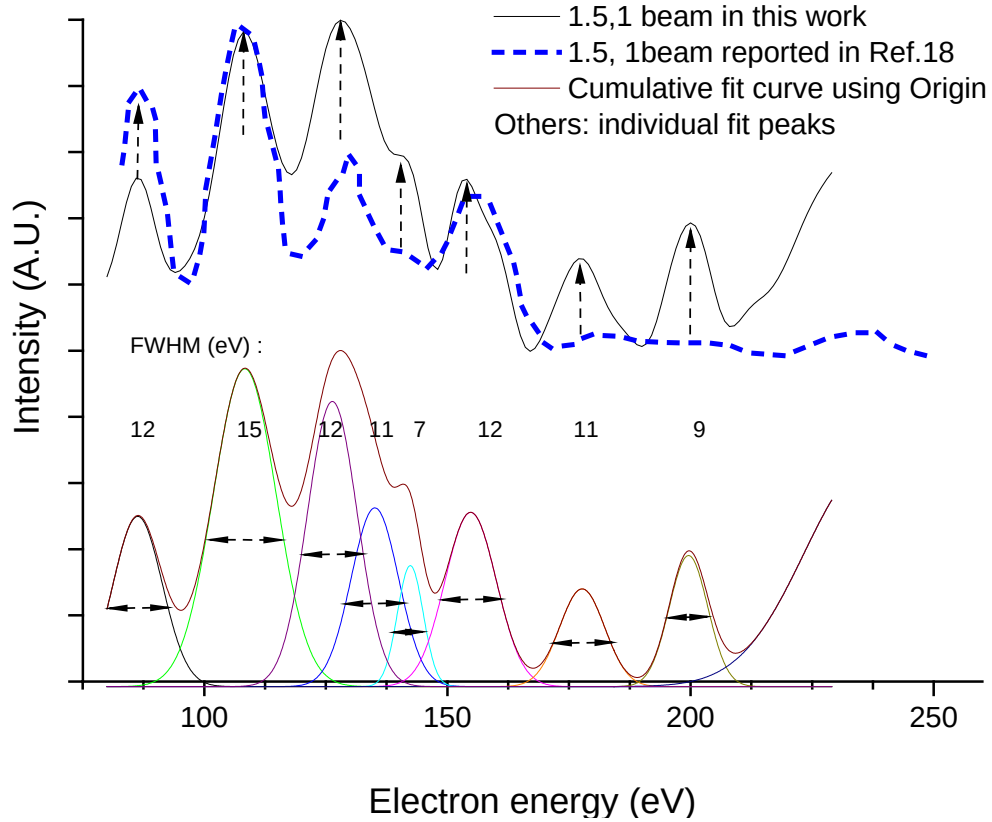


Figure 4.8 The comparison for I-V curves of (1.5, 1) spot between this work and Ref. 18 (upper) and peak width analysis by peak fitting (lower)

However, there are significant discrepancies in peak intensity. The peaks at 68 eV, 129 eV, 178 eV and 203 eV in this work are higher than those in Ref.18. It is partially caused by the reasons we have discussed in Sec. 4.1: With different experiment parameters such as the exposure time under the high energy electrons and the current of anode filament, the decay of beam intensity and the flux of incident beam may not be identical in two experiments. They can affect the contrast of the diffraction beams and the background so that the intensity measurements are deviated from the accurate value in different ways. The other possibilities are the different experimental temperatures and the

focusing abilities of the electron guns used in the experiments. LT at which LEED was performed in this work can improve the contrast of beams above 100 eV incident electron energy [40]. However, the data reported in Ref. 18 was recorded at room temperature. Different focusing ability of electron guns can cause a varying size of diffraction spots from low energy to high energy. It therefore changes the average intensity of spot per unit area, which is measured as the intensity of I-V curves. Furthermore, it is common that the maximal brightness of a diffraction spot exceeds the saturation intensity for a CCD camera. In the image, the intensity of those brighter area in a spot may be truncated and replaced with a saturated value, which is determined by the specification of the camera. When using another camera, the intensity of the peaks in I-V curves, corresponding to those brightest area, may be recorded discrepantly. At last, it is well-known that the reduction condition of TiO_2 is history dependent [2]. The specimens used in this work and in Ref. 18 might be quite different in concentration of defects such as O vacancies, Ti interstitials and step edges. Their different reduction conditions may have also caused the discrepant peak intensities.

By iterative calculation (See Fig. 3.6), the final structure is obtained with $R_p = 0.51$. The large value of the R_p suggests an indefinite correlation between the experimental spectra and the optimized structure. The theoretical I-V curves are plotted and compared to the experimental ones in Fig. 4.9. Significant discrepancies between theoretical peak positions and the experimental ones can be observed. The I-V comparison of (1, 1.5) spot

between theoretical and experimental spectra is shown. An experimental minimum is at 120 eV, but the calculated curve could not account for the peak. For the experimental

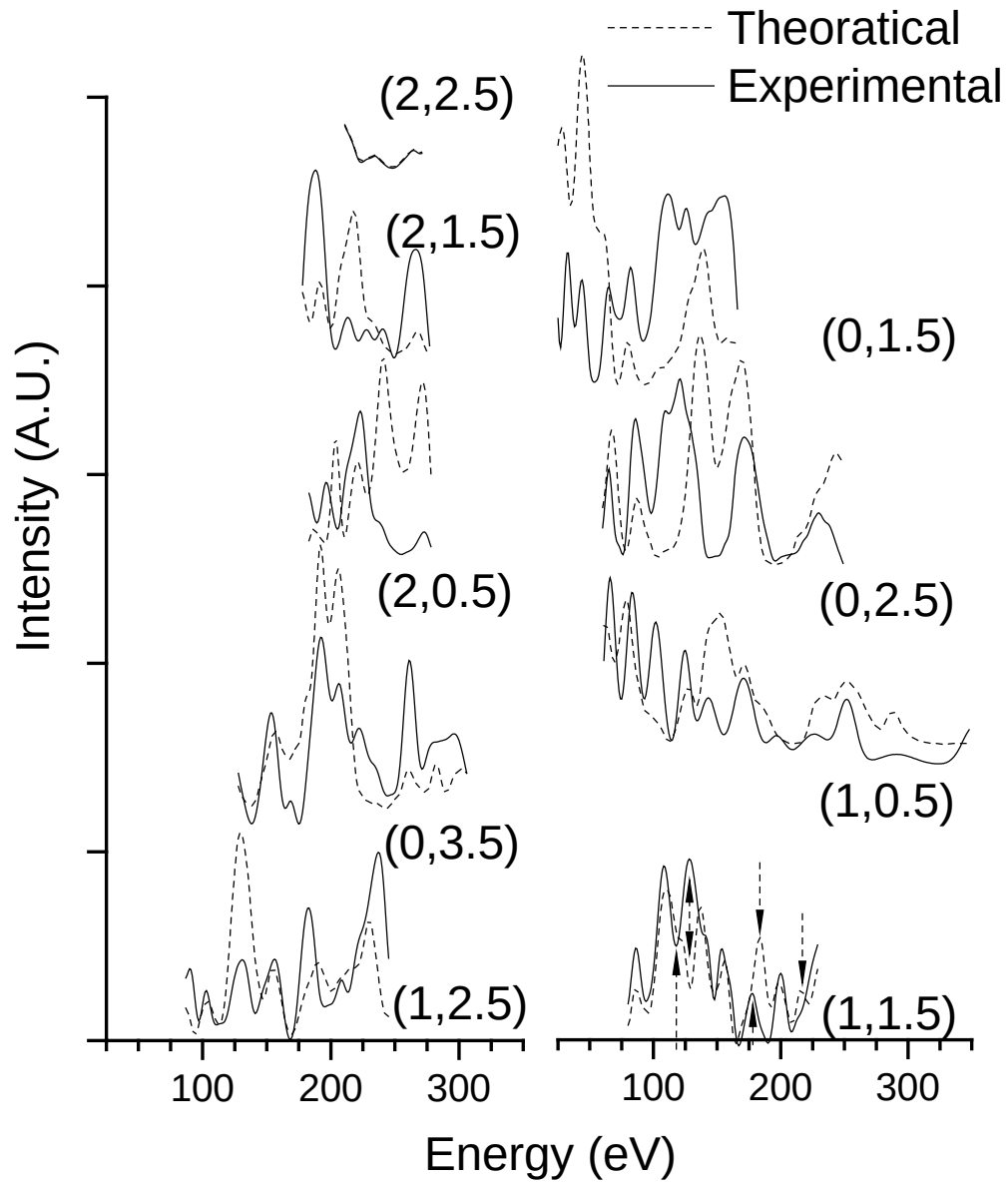


Figure 4.9 Comparison of theoretical and experimental I-V curves for (1x2) TiO_2 (upward arrow - experimental maxima or minima; downward arrow - theoretical maxima or minima)

maximum at 129 eV, the theoretical curve predicts a minimum instead. The experimental peak at 178 eV totally mismatches with the theoretical maximum 190 eV. Additionally, the theoretical maximum at 223 eV misses its experimental counterpart at all. All these missing or mismatched spectral maxima and minima contribute to the large value of the average R_p .

As an attempt to lower the R_p value, the different Debye temperatures are sought for better handling for different elements in the structure. They have been optimized to 300 K and 370 K for oxygen and titanium, respectively (searching from 100K to 1000K in a grid of 10 K), but it has not made significant improvement in R_p . Two Debye temperatures are searched and used for the surface atoms (#1 - 13) apart from those beneath, but the effort didn't improve the result.

The optimized structure is shown with the numbered atoms and the bond distances in Fig. 4.10. The atomic coordinates are listed in Table 4.3, and the files used to generate the final structure are listed in Appx. C. The bond lengths are not compared with those from the DFT calculation of Ti_2O added row model because the high R_p value indicates a poor correlation to the physical structure. Such poor correlation can be gleaned from large deviations of bond distances (Fig. 4.10). For example, the bond distance between the O #21 and the Ti #25 is drastically elongated by 0.39 Å from its bulk value, 1.983 Å. On the other hand, the bond between the Ti # 2 or 3 and the O #6 or 7 is contracted astonishingly to 1.309 Å.

Table 4.3 Optimized structure coordinates for (1x2) reconstructed TiO₂(110)

Element	#	Z(Å)	X(Å)	Y(Å)
O	1	0	0	0
Ti	2	0.2687	-1.1339	1.479
Ti	3	0.2687	1.1339	1.479
O	4	0.5764	-1.9737	0
O	5	0.5764	1.9737	0
O	6	1.36	5.3919	1.479
O	7	1.36	-5.3919	1.479
O	8	1.5738	-1.2344	1.479
O	9	1.5738	1.2344	1.479
Ti	10	1.6624	3.0241	1.479
Ti	11	1.6624	-3.0241	1.479
Ti	12	1.8019	6.496	0
Ti	13	1.9013	0	0
O	14	3.3731	-2.7915	0
O	15	3.3731	2.7915	0
O	16	3.952	0	0
O	17	4.0343	6.496	0
O	18	5.0211	2.1042	1.479
O	19	5.0211	-2.1042	1.479
Ti	20	5.2965	0	1.479
Ti	21	4.9695	-3.3735	0
Ti	22	4.9695	3.3735	0
O	23	5.4352	-4.1127	1.479
O	24	5.4352	4.1127	1.479
Ti	25	5.5344	6.496	1.479
O	26	6.0314	0	0
O	27	6.4957	6.496	0
O	28	7.0545	3.2237	0
O	29	7.0545	-3.2237	0

understand the failure to find the structure correlated to the experimental LEED data, the details in modeling need to be carefully reviewed. In Fig. 4.10, the optimizable atoms in model has been divided into two layers (gray dashed line) below (1x2) Ti_2O added row and the bridging oxygens. The distance between layers along $[110]$ is about one lattice constant ($\sim 3.2 \text{ \AA}$, may change due to relaxation). The optimizable atoms in this work are modeled down to the second layer (Fig. 4.7), and that in Ref. 18 is only down to the first layer. In the both works, the structures below these layers are assumed to be bulk. Such an inadequate assumption may severely limit the simulation result so that the algorithm overdrives the movement of optimizable layers in search for the minimizing R_p .

The importance of optimizing the atoms in deeper layers can be gleaned from the previous study of (1x1) TiO_2 . For the atoms from the deeper layer in (1x1) optimized structure (Fig. 4.5, Tab. 4.1, atom # 14 - 25), the displacements from bulk positions are still noticeable as 0.04 - 0.08 $\text{\AA}$. The modeling depth for these atoms would be equivalent to the fourth layer in the (1x2) structure.

A recent study by Lindsay *et. al.* [12] highlights the importance of including a sufficient number of optimizable layers in SPALeED of (1x1) TiO_2 relaxation. It shows, the resultant structures of SXRD and LEED analyses agree with each other and generates a satisfactory R_p value of 0.2 when their models includes five optimizable layers. However, the two methods give discrepant results, and the R_p can only be optimized to an unsatisfactory value of 0.4 when the number of optimizable layers in the model is limited

to two. This study suggests that modeling with limited optimizable layers in LEED analysis may cause discrepancy of the resultant structure from the physically consistent one, or from the result of another analyses (*e. g.* discrepant result of LEED & SXRD). Similarly in the (1x2) reconstruction studies in this work and Ref. 18, the LEED calculation results may also be limited by inadequate optimizable layers in the models. It is noteworthy that, M. Blanco *et. al.* performed a LEED study of Ti_2O_3 added row model (see Fig. 1.6), which only models with one optimizable layer but obtains a low R_p value as 0.28. However in the view of Lindsay's study, a resultant structure with insufficient optimizable layers should be trusted with caution.

In summary, the LEED calculation of Ti_2O , which best fits spectra of fractional spots more sensitive to (1x2) surface, generates a R_p value similar to what is reported in literature [18]. It is believed that the high value of the resultant R_p is in part due to an insufficient number of optimizable layers in the model. To remedy the deficiency and include more optimizable layers, additional atoms with their degrees of search freedom need to be included. It also means a larger energy range of the experimental spectra is necessary to satisfy the reliable energy range per search freedom (normally 50 eV). For example, modeling Ti_2O added row to the fourth optimizable layers needs 50 degrees of search freedom, which mean one extra thousand electron volt range of the experimental I-V curves for the fractional spots. Thus, refined experimental instruments should be applied for extracting a larger amount of quality data for extending the range of higher

energy I-V curves. Enhanced sharpness and contrast of diffraction spots are essential for this purpose. Lower temperature cryogenics to further reduce the thermal vibration, an electron gun capable of sharper beam and a complete magnetic shield to remove beam oscillation should be used. In addition, the sharper diffraction spots should enable a more reliable measurement in intensity particularly at higher energy as neighboring spots are spatially better resolved (see Fig. 1.5, right). At last, a higher sensitive camera should be helpful to detect the weak diffraction spots in presence of high background.

4.3 Carbon-Carbon Coupling of Formaldehyde on Partial Reduced (1x1) TiO₂(110)

Chemical bonds and reactions are essentially caused by interactions among outer shell electrons of atoms. Because these electrons can tunnel vacuum barrier to STM, STM is therefore capable of imaging chemical bonding between molecules in molecular resolution, and is a powerful tool for investigation of such bonds and reactions. In this study, the carbon-carbon coupling of formaldehyde on reduced (1x1) TiO₂ surface is examined using STM. To understand empty state STM images of TiO₂(110) in an ordinary experimental conditions, an atomically resolved STM image of the same area can be used as a reference map. Atomically resolved images show the 5-fold coordinated Ti atoms as a grid of bright protrusions (Fig. 4.11a). In the STM images with ordinary resolution, these 5-fold coordinated Ti atoms appear as bright lines along [001] (Fig. 4.11b) rather than protruded dots. By identifying the 5-fold coordinated

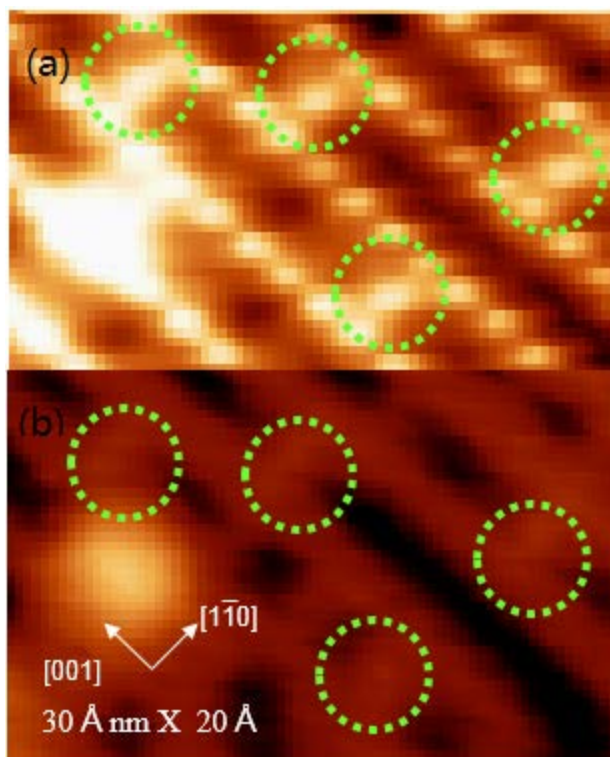


Figure 4.11 (a) STM images of atomic resolution and (b) ordinary resolution of $\text{TiO}_2(110)$

Ti sites in both images, the sites of bridging oxygen – O_b can be mapped between two chains of bright dots or between two bright lines. On this surface, the most studied defects are bridging oxygen vacancy (V_O , Fig. 1.3, dashed circle) [2, 21]. Because V_O exposes 5-fold coordinated Ti underneath, they are imaged as a bright dot on the O_b sites between two 5-fold coordinated Ti chains in both the images (Fig. 4.11a & b; bright dots in green dashed circles). The dangling bonds resulted from V_O [2] can exhibit enhanced chemical reactivity toward various organic molecules including formaldehyde, acetone and ethanol [22-25]. $\text{TiO}_2(110)$ containing V_O hereby provides a model system for

studying the catalytic properties of the surface toward the organic molecules with C = O group.

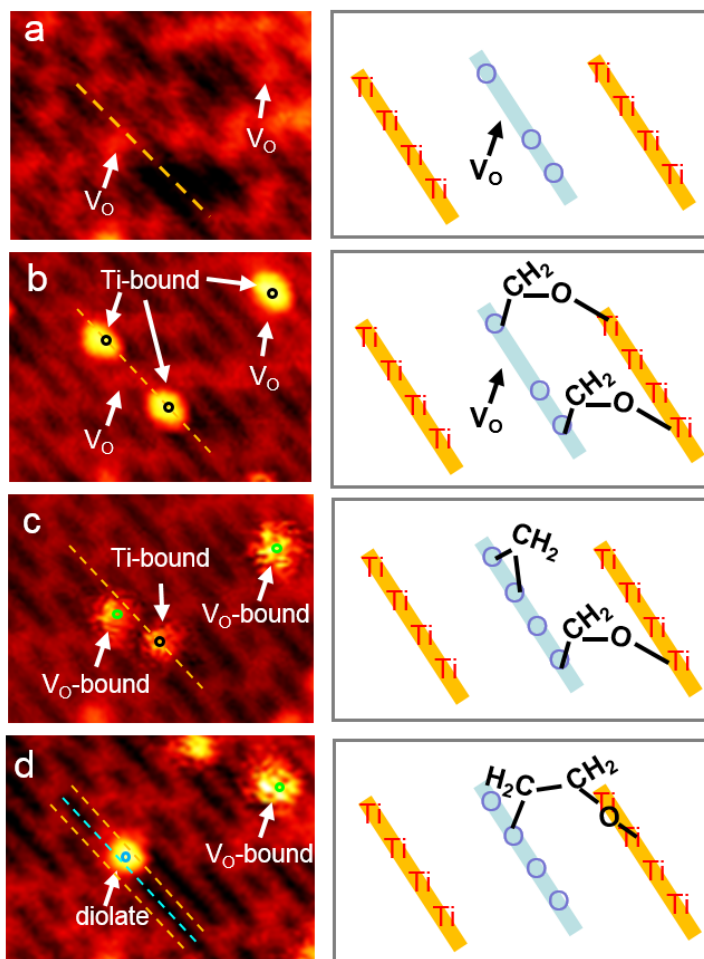


Figure 4.12 STM images obtained from the same area of reduced $\text{TiO}_2(110)$ at different temperatures, revealing the formation of diolate via coupling of the Ti-bound formaldehyde and the V_O -bound formaldehyde: (a) clean surface imaged at 75 K, (b) surface imaged at 75 K after dosing 0.02 ML formaldehyde at 75 K ($V_\text{b} = 1.3$ V), (c) imaged at 145 K ($V_\text{b} = 1.5$ V) after subsequently increasing the temperature of b to 145 K, and (d) imaged at 170 K ($V_\text{b} = 1.3$ V). Dotted lines mark the position of Ti rows (orange) and O_b row (blue). An additional example is provided in the SI as Figure S1 in Appx. D.

The adsorption of formaldehyde on reduced $\text{TiO}_2(110)$ was carried out at 75 K (Fig. 4.12 a & b). The interaction between formaldehyde and (110) was imaged and studied using variable temperature (VT) STM. Following reactions of individual molecules as a function of increasing temperatures ranging from 75 K to 310 K can provide the detailed bonding and site-specific reaction information. Particularly by increasing the temperature incrementally and following the same set of formaldehyde molecules, one can directly observe individual chemical reactions, the formation of a stable species, and the role of the defects.

After formaldehyde exposure, Ti-bound $\text{CH}_2\text{O}_{\text{Ti}}$ molecules (Fig. 4.12b, black circles) appear as bright features on Ti row (dotted orange line) at 75 K at a typical bias voltage of ~ 1.3 V. At low bias voltage (~ 0.9 V), it centers between Ti row and O_b row. $\text{CH}_2\text{O}_{\text{Ti}}$ stays immobile until the temperature increases to ~ 110 K, at which $\text{CH}_2\text{O}_{\text{Ti}}$ starts to diffuse along the Ti row. Most of the molecules end up adsorbed on V_O 's as a fuzzy V_O -centered CH_2O feature [23]. As shown in the image taken at 145 K (Fig. 4.12c), two of the $\text{CH}_2\text{O}_{\text{Ti}}$ molecules move to nearby V_O sites and appear as fuzzy V_O -bound CH_2O features (green circles). The other $\text{CH}_2\text{O}_{\text{Ti}}$ (black circle) is still located at its original position on Ti row. Its less-defined appearance is due to the bias voltage and the tip status [23].

After the temperature is increased to 170 K, the same area image shows that the $\text{CH}_2\text{O}_{\text{Ti}}$ (Fig. 4.12c, black circle) reacts with the nearby V_O -bound CH_2O and forms a

bright feature (Fig. 4.12d, blue circle). A close inspection reveals that the bright feature is off-centered from the O_b row (blue dotted line). It is assigned as diolate species ($-OCH_2CH_2O-$) formed via carbon-carbon coupling.

Formation of diolate was previously proposed by Qiu *et. al.* [25] They observed the typical HREELS loss peaks of the diolate instead of that of the $C=O$ bond when they characterized the chemisorbed HCHO species on defective $TiO_2(110)$ surface at room temperature. They proposed that the diolate species could form through activation of two formaldehyde molecules adsorbed at the adjacent V_O sites. By following the same set of molecules, our STM images clearly show that the formation of the diolate involves one Ti-bound CH_2O_{Ti} and one V_O -bound CH_2O and the position of the resulting diolate is between the O_b row and the neighboring Ti row. Therefore the diolate most likely bonds to the Ti row via an oxygen atom and also to the O_b row via another oxygen atom, forming a carbon-carbon bond in the middle as shown in the ball model for Fig. 4.12d.

The possibility of paraformaldehyde also has been considered as it was suggested as the dominant species from HREELS study on perfect surfaces at low temperature (110 K) [26]. The diolate species observed in STM images is formed from one V_O -bound CH_2O and one Ti-bound CH_2O . Thus, it is unlikely to be the paraformaldehyde identified on pristine surfaces. In addition, to form paraformaldehyde commonly observed on metal surfaces [57] from these two formaldehyde molecules, one additional oxygen presumably from H_2O is needed. Therefore the possibility of paraformaldehyde is excluded and the

species is assigned as diolate. Similar diolate species have been observed following the reaction of ethylene glycol with V_O 's and subsequent deprotonation of their Ti-bound hydroxyl group [58, 59].

It is worth noting that the existence of another V_O -bound fuzzy CH_2O feature (Fig. 4.12d, green circle) formed at the upper right hand corner of the same image, clearly distinguishes the V_O -bound CH_2O from the bright diolate feature. To quantitatively differentiate the observed features, the average apparent height of V_O -bound CH_2O and that of the off-centered diolate relative to the neighboring Ti row are measured on a $35 \times 35 \text{ nm}^2$ image taken with a bias voltage of 1.3 V. The height of diolate relative to the Ti row is $1.7 \pm 0.1 \text{ \AA}$, which is much higher than $1.0 \pm 0.1 \text{ \AA}$ measured for the V_O -bound CH_2O . In addition, unlike V_O -bound CH_2O , which becomes mobile at temperature above 170 K [23]. These diolate features are not mobile throughout the temperature range that we examined ($< 310 \text{ K}$).

Statistical analysis on large areas ($35 \times 35 \text{ nm}^2$) obtained from eight separate experiments show that only $\sim 10\%$ of surface species appear as diolate species at 75 K and the percentage slowly increases to $\sim 20\%$ at 170 K at low coverage ($\sim 0.02 \text{ ML}$) employed here. The majority of unreacted formaldehyde molecules are V_O -bound CH_2O . We believe that the diolate yield at 170 K is limited by mobility of the V_O -bound CH_2O and limited supply of CH_2O_{Ti} . The formation of diolate is a secondary reaction, which requires a Ti-bound CH_2O_{Ti} encountering a V_O -bound CH_2O , a reaction product of a

Ti-bound CH_2O reacting with a V_O site. At 170 K, most of the Ti-bound formaldehyde are mobile on Ti row with a low diffusion barrier ($E_b = 0.2\text{--}0.3$ eV) while most of the V_O -bound formaldehyde molecules just started to diffuse along the O_b row as methylene group ($E_b = 0.4\text{--}0.5$ eV) [23]. Therefore, the probability of Ti-bound formaldehyde molecule encountering an empty V_O sites (~ 0.13 ML) and forming V_O -bound CH_2O is at least an order of magnitude higher than the probability of reaction with a newly formed V_O -bound CH_2O forming diolate at the low CH_2O exposure (~ 0.02 ML) employed here.

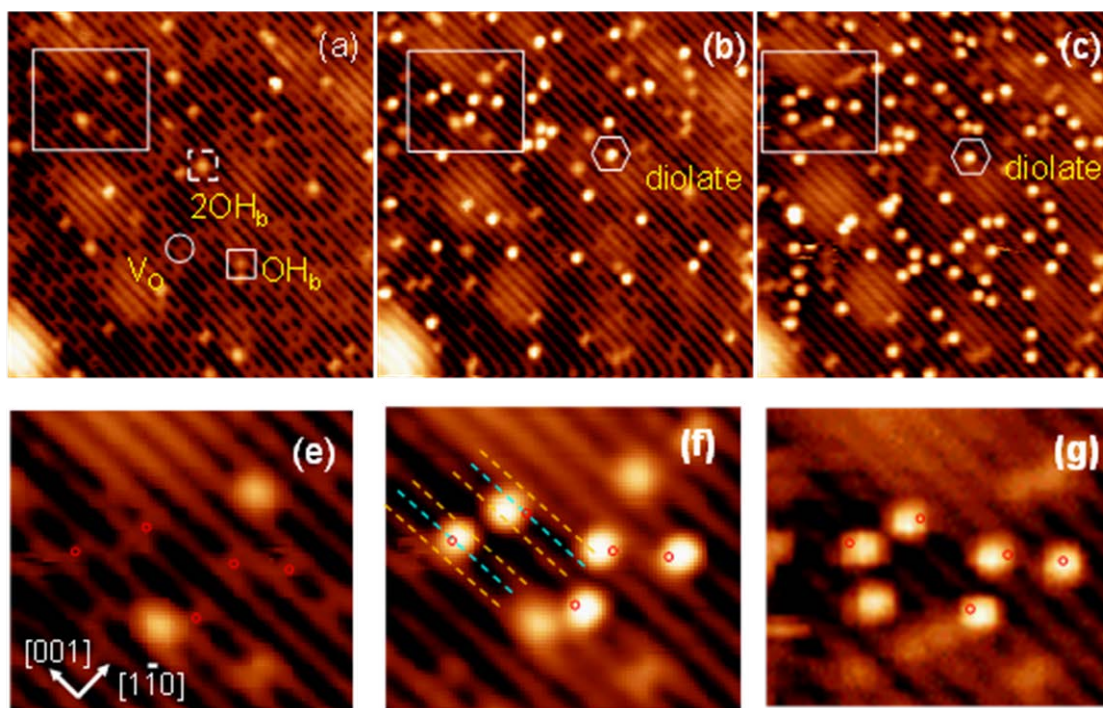


Figure 4.13 (a-f) STM images from the same area ($200 \times 200 \text{ \AA}^2$) of a reduced TiO_2 (110) surface before and after exposure of formaldehyde at room temperature: (a) clean surface; (b) surface after first exposure; (c) after second exposure; (e, f, and g) magnified areas marked in (a, b, and c). Red circles mark the position of V_O 's. Dotted lines mark the position of Ti rows (orange) and O_b rows (blue)

In order to investigate surface species formed upon an adsorption of formaldehyde on $\text{TiO}_2(110)$ at room temperature, an area of $20 \times 20 \text{ nm}^2$ was monitored and compared before and after exposure. Fig. 4.13a shows a clean surface of reduced $\text{TiO}_2(110)$. The concentration of V_O is determined to be 0.10 ML. In addition to V_O , the reduced $\text{TiO}_2(110)$ in Fig. 4.13a shows a small amount of bridging hydroxyl species (OH_b) as a result of background water adsorption in V_O [21]. Upon the exposure of the surface to formaldehyde, the most significant change in the same area (Fig. 4.13b) is the appearance of bright features - the assigned diolates. The coverage of the bright features is determined as 0.02 ML.

A closer examination reveals that these bright features are centered between O_b rows and Ti rows (Fig. 4.13f). They are either slightly above or below the O_b rows (Fig. 4.13f, blue dotted lines). The appearance and the measured apparent height of these off-centered bright species are consistent with the observed diolate at low temperature (Fig. 4.13d). Comparison of same areas (*e. g.* Fig. 4.13e and 4.13f) among four different experiments shows over 80% of them are located either right on a V_O site or on the nearest neighboring site of V_O (red circles). This observation supports the involvement of V_O sites in the formation of diolates.

At room temperature, the V_O -bound formaldehyde can diffuse via two diffusion channels. One is the diffusion along the O_b row as $-\text{CH}_2-$ with an estimated diffusion barrier (E_b) of 0.4–0.5 eV and the other is moving from V_O site to Ti row ($E_\text{b} = 0.6\text{--}0.7 \text{ eV}$)

and diffusing along Ti row as a Ti-bound CH_2O ($E_b = 0.2\text{--}0.3$ eV) [23]. The diffusion rate ($\sim 10^8 \text{ s}^{-1}$) of Ti-bound $\text{CH}_2\text{O}_{\text{Ti}}$ at room temperature is estimated to be at least 6 orders of magnitude higher than the rate of V_O -bound CH_2O moving out of a V_O site using the Arrhenius dependence. Therefore, upon exposure, most of the Ti-bound CH_2O molecules react with V_O sites forming V_O -bound CH_2O species. However, newly formed V_O -bound CH_2O can move out from the V_O site with a rate of $\sim 10^2 \text{ s}^{-1}$ and diffuses along Ti row as a Ti-bound $\text{CH}_2\text{O}_{\text{Ti}}$, which further reacts with V_O -bound CH_2O forming diolate. In the meantime, the combination of the two V_O -bound CH_2O diffusion channels could shift the position of V_O -bound CH_2O from the original V_O site. Therefore it is reasonable to assume that a small amount ($\sim 20\%$) of diolates, which are displaced from the original V_O position are formed from V_O -bound CH_2O moving out from V_O sites and reacting with the shifted V_O -bound CH_2O . As one additional diffusion channel is involved, the probability is low. We have not observed V_O -bound fuzzy CH_2O indicating that they all converted to other species at room temperature.

After additional formaldehyde exposure (Fig. 4.13c), the coverage of these bright off-centered diolate features increases to 0.04 ML. The comparison of Fig. 4.13f and g shows that the diolate species are stationary at room temperature, which is similar to the stability of diolates formed from diol molecules on reduce $\text{TiO}_2(110)$ [58, 59]. They are much more stable than the Ti-bound formaldehyde in the similar configuration. One possible reason is the difference in the diffusion processes. The diffusion of Ti-bound

CH₂O is via changing its configuration from η^2 (O_{Ti},C_{Ob})-dioxymethylene to η^1 Ti-straight formaldehyde and then diffusing along Ti row as η^1 Ti-straight formaldehyde [23]. As for the diffusion of a diolate species, it would require the displacement of both ends that bind to O_b and Ti simultaneously. Consequently, Ti-CH₂O is mobile even at 110 K while the diolate species were not activated until a much higher temperature. Additional theoretical calculation is needed to quantify the energetics.

Benz *et. al.* reported that the Ti interstitials promote the formation of diolate in the coupling reaction of benzaldehyde on TiO₂(110). In their report, benzaldehyde molecules distribute randomly on Ti row in the STM images and none of the benzaldehyde molecules were observed over V_O sites [28]. Here, our results clearly show that the formation of the diolate from formaldehyde molecules involves one V_O-bound CH₂O and one Ti-bound CH₂O_{Ti}. There is no evidence for the involvement of Ti interstitials in the formation of formaldehyde diolate species.

The formation of diolate species was further examined through statistical analysis performed on isothermal images after two different experimental methods of exposing a TiO₂(110) surface to formaldehyde (Fig. 4.14) at 190 K. In the first set of experiments (Sequence A), after TiO₂(110) was exposed to formaldehyde, the doser and the chamber were evacuated to stop dosing. Then the surface were monitored in an area of 150 × 150 Å². Immediately after the exposure, the surface has 0.10 ML unoccupied V_O and 0.025 ML V_O-bound CH₂O. Negligible CH₂O_{Ti} is observed as expected at this temperature. The

isothermal images show that the diolate species has a negligible increase during the period of 52 minutes (Sequence A) as there is little $\text{CH}_2\text{O}_{\text{Ti}}$ available to react with V_O -bound CH_2O at the small exposure of only 0.025 ML CH_2O . The concentration of V_O decreases slightly by 0.015 ML during this period. In the meantime, the number of V_O -bound CH_2O decreases from 0.025 ML to almost zero due to a minor reaction channel, formation of methyl [31].

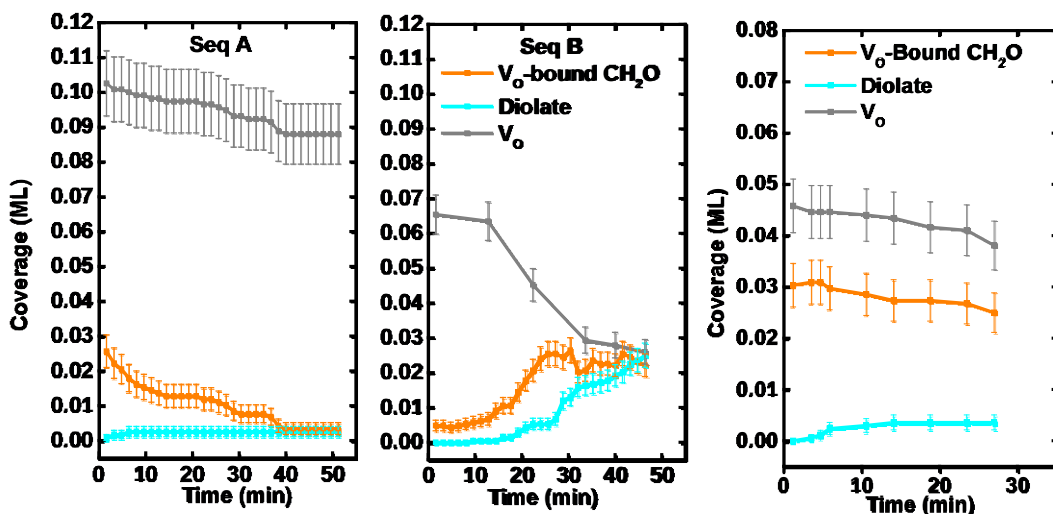


Figure 4.14 The time dependence of coverage for various surface species on isothermal images taken at 190 K with two different methods of exposing a $\text{TiO}_2(110)$ surface to formaldehyde. Sequence A is taken after CH_2O exposure. Sequence B is taken with continuous CH_2O exposure. The figure on the right shows a species coverage of another control group applies same experiment method of Seq. A. With increase V_O -Bound, the diolate formation remains the same trend as Seq A.

Another set of statistical analysis (Fig. 4.14, right) performed on a surface with less V_O -concentration (0.075 ML) shows the similar time dependence of the coverages of V_O ,

V_O -bound CH_2O , and diolates at 180 K. Its comparison versus Seq. A demonstrate a change in species coverage does not effect the formation of diolate.

In the experiments (Sequence B) as control group, surface species were monitored isothermally on an area of $200 \times 200 \text{ \AA}^2$ while the surface was continuously dosed with formaldehyde molecules at 190 K. During the same period (48 minutes), the concentration of V_O drops significantly from 0.065 ML to 0.025 ML. The large decrease is countered by an increase of both V_O -bound CH_2O and diolate species: from 0.005 ML to 0.02 ML and from 0.01 ML to 0.025 ML, respectively. The isothermal movie clearly shows that the numerical rise of V_O -bound CH_2O is because the continuously supplied CH_2O molecules adsorb at the V_O sites as expected. Likewise, the continuously supplied CH_2O_{Ti} molecules are also directly responsible for the numerical increase of the off-centered diolate species. The contrast between Sequence A and B clearly shows that the formation of the diolate species requires both CH_2O_{Ti} and V_O -bound CH_2O :



with the continuously supplied CH_2O molecules in Sequence B, the rate of Reaction for Eq. 4.3 increases with the increasing of the concentration of V_O-CH_2O as shown in Fig. 4.14. The observed decreasing of V_O (0.04 ML) is consistent with the expected total consumption of V_O in forming 0.015 ML V_O -bound CH_2O (Eq. 4.2) and 0.025 ML of diolate species (Eq 4.2 and Eq 4.3).

Reports from two different groups indicated that the formaldehyde species that bound on V_O sites lead to the formation of C_2H_4 desorption peak at ~ 620 K [25, 60]. Both groups did the TPD experiments after partial blocking of V_O sites with H_2O molecules and reported the suppression the formation of the C_2H_4 yield at high temperature. Therefore the high temperature peak has been assigned as the reductive reactions between two V_O -bound CH_2O molecules. Most recent XPS study by Yuan *et. al.* reports that the V_O -related species observed at room temperature with a C bonding energy of 289.6 eV, convert to species with a C bonding energy of 286.6 eV at ~ 450 K [60]. The 289.6 eV species was assigned as $\eta^2(O_{Vo}, C_{Obr})$ -dioxymethylene species and the 286.6 eV species are assigned as diolates, which are stable up 600 K and eventually yield C_2H_4 . Our STM data clearly show that the V_O -related species observed at room temperature are not isolated CH_2O molecules. Majority species that we observe at room temperature are the diolate species formed via coupling of Ti-bound and V_O -bound CH_2O molecules. Our STM results suggest the high temperature peak could be the breaking of two carbon-oxygen bonds of the diolate species. The mechanism of formation of ethylene is similar to the reactions observed on the single crystal V(110) [61], on which the high-temperature ethylene requires the prior formation of the intermediate $-OCH_2CH_2O-$ diolate. We do not exclude the possibility that the diolate species can further react and convert to another intermediate that is stable at higher temperature. The production of propylene from diolates formed from 1, 3-propene diols on

reduced $\text{TiO}_2(110)$ proceeds via the conversion of the diolate to a new diolate species at ~ 400 K following by the sequential breaking of the C-O bond at ~ 600 K [58].

4.4 Adsorption of Trimethyl Acetic Acid on Cross-linked (1x2) $\text{TiO}_2(110)$

In this work, the adsorption of trimethyl acetic acid ($(\text{CH}_3)_3\text{CCOOH}$, TMAA) on a (1x2) reconstructed rutile $\text{TiO}_2(110)$ is investigated using STM. The comparison of the same area before and after various exposures to TMAA is used to gain insights into the interaction between carboxylic acids on a partially reduced TiO_2 surface. In addition, the three specific atomistic models for the (1x2) reconstruction (Fig. 1.6) are compared and contrasted to experimentally observed adsorption behaviors of TMAA.

TMAA was introduced onto the $\text{TiO}_2(110)$ surface at the STM stage via a retractable tube doser. Prior to actual dosing of TMAA to the surface, TMAA was cleaned by flash up to 900 K. All STM images (empty states) were collected in a constant-current (0.3 nA) mode at positive sample bias voltages ($V_{\text{bias}} = 1.0$ V). The coverages of adsorbed molecules at various states were obtained by a direct count in STM images and expressed in monolayer (ML) units (1 ML corresponds to $5.2 \times 10^{14} \text{ cm}^{-2}$ Ti atoms).

Fig. 4.15 shows the images of the same area on (1x2) $\text{TiO}_2(110)$ before and after the exposure of TMAA molecules. Prior to the adsorption of TMAA, the (1x2) reconstructed surface exhibits the characteristic strands running along [001]. The spacing between two adjacent strands is well established as 13 Å [2], so the value along with the lattice constants from (1x1) surface is used as an internal calibration for the study. The reduced surface also

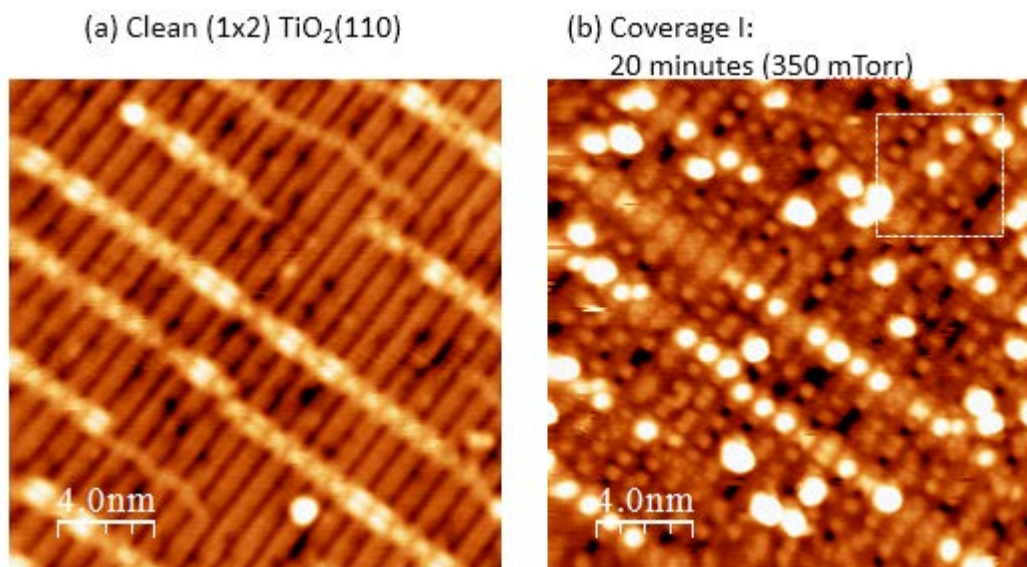


Figure 4.15 Two consecutive STM images are taken from a same area at room temperature. (a) clean (1x2) $\text{TiO}_2(110)$ with cross-links, (b) The coverage I after an exposure to TMAA at 350 mTorr for 20 minutes.

shows cross-links running along $[110]$. Most of them have the average FWHM of $6.5 \text{ \AA}$, spanning about two lattice constants along $[001]$, thus they are labeled as double strands. Some of the strands are only half in thickness, compared to the double strands therefore designated as single strands.

After the exposure to 350 mTorr of TMAA for 20 minutes, the same area reveals numerous bright features adsorbed on various surface sites (Fig. 4.15b). The majority of TMAA appears in trough, in-between two adjacent (1x2) strands. Under the bias condition used, they are measured $1.5 \text{ \AA}$ in height and $5.7 \text{ \AA}$ in FWHM.

On one hand, the molecules form a chain as a near-saturated coverage in most of troughs. These TMAA molecules are close-packed along each trough. The nearest

neighbor distance between TMAA molecules in through is measured as 6 Å in average, corresponding to two lattice constants along [001]. There are gaps or vacancies visible occasionally in troughs although some of the vacancies could actually be impurities affecting tip imaging. In the other troughs, some of them are observed isolated. Also, some other molecules are aligned in pairs along [110]. On the other hand, there are only a few adsorbates observed on the (1x2) strands themselves. In addition to the troughs, the crosslinks show a number of TMAA molecules adsorbed. They are about 1.5 Å in height and 6.5 Å in FWHM similar to those adsorbed in troughs. In addition, they form lines perpendicular to the molecular chains in troughs providing an easy marker for the same area comparison.

Similar to the finding in the coverage dependence study of TMAA adsorption on (1x2) TiO₂ [62], a clear adsorption preference of TMAA to adsorb in a trough over a (1x2) strand by TMAA can be observed in Fig. 4.15b. Such preference is by now palpable as the close-packed molecules form quasi-one dimensional chains well separated by (1x2) strands. The areas where the less TMAA molecules are adsorbed on (1x2) strands, are easily discernable with a bright contrast, consistent with the topographically higher position compared to the trough position. Some adsorbates appear in a single molecule in shape and size whereas others apparently form a cluster of two or more molecules.

The TMAA coverages are calculated first by measuring the areas of distinctive sites adsorbed by the molecules: in troughs between two adjacent strands, on top of the

crosslinks and strands. Each covered area is then subsequently normalized to monolayer (ML), where 1 ML is defined as one molecule per the (1x1) unit cell of TiO₂(110) - 3.0 Å x 6.5 Å. For close-packed molecules in troughs on (1x2) reconstructed surface, the unit cell is about 6.0 Å x 13.0 Å or 2x2 unit cell, thus the saturation coverage is 0.25 ML. The saturation coverage for strands should be the same 0.25 ML too since it represents an alternate site in the same 2x2 unit cell. For the crosslinks (double only), the unit cell area is estimated as 9.0 Å x 13.0 Å or 3x2 unit cell, and the saturation on crosslinks should be 0.167ML. For TMAA adsorbed on various sites after each exposure, the calculated ML coverages are shown in Table 4.4. The most occupied site (54.6%) is crosslink with a coverage of 0.091 ML. The trough site is in a comparable occupation (44.8%) with a coverage of 0.112 ML. And, the coverage data shows that the strand is the least favorable adsorption site (4.8%, 0.012 ML) for TMAA among the three sites.

Table 4.4 Coverage of TMAA adsorption on clean (1x2) TiO₂(110)

TMAA adsorption	Coverage I in ML (percentage)
Trough	0.112 ML (44.8%)
Strands	0.012 ML (4.8%)
Crosslink	0.091 ML (54.6%)

Figure 4.16a&b are close-up views of close-packed assembly of TMAA molecules formed on (1x2) and (1x1) surfaces, respectively. The TMAA molecules are lined up in the

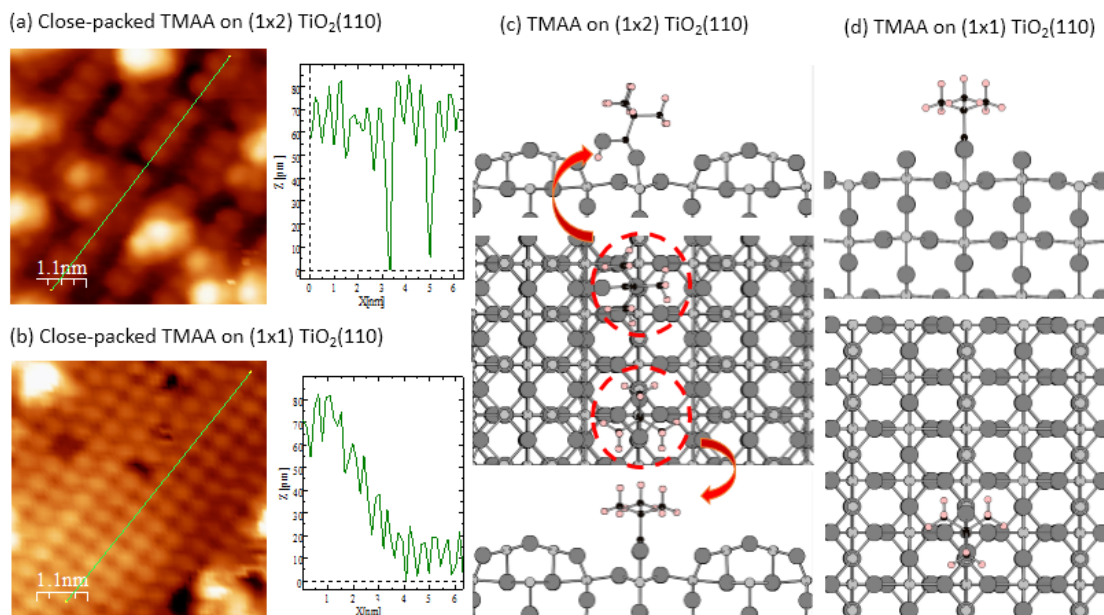


Figure 4.16 Close-up views of close-packed TMAA on (a) (1x2) $\text{TiO}_2(110)$ and (b) (1x1) $\text{TiO}_2(110)$. The height profiles along the green lines are also shown for comparison. (c) Proposed, qualitative bonding geometry for physisorbed TMAA in troughs on (1x2) $\text{TiO}_2(110)$ (top: side view, middle: top view) and for de-protonated TMA in bi-dentate configuration (bottom: side view, middle: top view), and (d) de-protonated TMA on (1x1) $\text{TiO}_2(110)$. For TMAA, oxygen, carbon, and hydrogen atoms are shown as pink, black, and beige spheres.

trough of (1x2) reconstructed surface with the nearest neighbor distance of 6 Å in average (Fig. 4.16a). The measured value is exactly the same as that measured on (1x1) surface along [001] (Fig. 4.16b). The TMAA molecular chains in adjacent troughs on (1x2) surface do not appear to correlate with one another as the TMAA positions in adjacent chains are off by one lattice constant 3 Å along [110]. On (1x1) surface, the nearest neighbor distance along [110] is 6.5 Å, which is exactly one lattice constant of $\text{TiO}_2(110)$ along the direction. Thus the resulting unit cell for the TMAA overlayer is rectangular (albeit nearly

square-like). However, there are some domain boundaries, where two adjacent rectangular unit cells are shifted against one another by 3 Å along [001] (Fig. 4.16b).

The adsorption geometry of TMAA on (1x1) TiO₂(110) at 300 K is well established. TMAA adsorbs with its carboxylic group down and its tri-methyl groups away from the surface. It is also believed that the TMAA molecule de-protonates into trimethyl acetate (TMA, (CH₃)CCOO) and that the resulting TMA is bridge-bonded over two adjacent 5-fold coordinated Ti⁴⁺ sites. Such bonding geometry has been supported by density functional theory calculations as well as the observation of hydroxyl species nearby TMA adsorbed [30, 31, 63]. From the comparison in TMAA positions and nearest neighbor distance between (1x2) and (1x1) surfaces, it is evident that the TMAA molecules in troughs of (1x2) surface can adsorb similarly over two adjacent 5-fold coordinated Ti⁴⁺ sites in bi-dentate configuration as on (1x1) surface. Of the three (1x2) reconstructed models considered, the Ti₃O₆ structural model poses a serious conflict with experimental observation of TMAA adsorbing in trough because its trough is too deep and narrow to fit in between the two adjacent rows. In addition, the Ti₃O₆ model has 5-fold coordinated Ti⁴⁺ sites on top of the rows just as (1x1) TiO₂(110) (Fig. 1.6d), and those sites should be available for TMAA adsorption even before considering the trough space. The STM data clearly shows that TMAA preferably adsorbs in trough, thus it is concluded that the Ti₃O₆ model is not consistent with the observation. On the other hand, both Ti₂O₃ and Ti₂O row models have a trough wide and shallow enough for TMAA to adsorb easily. Figure 4.16c

(middle & bottom) shows schematics of such TMA adsorption geometry in the trough between Ti_2O rows, with the carboxylate group bridging above two 5-fold coordinated Ti^{4+} sites along [001].

Although de-protonated TMA in bi-dentate configuration is believed to be the most stable geometry on stoichiometric (1x1) $\text{TiO}_2(110)$ except the adsorption at oxygen vacancy, it is not entirely clear that the same is true on (1x2) reconstructed $\text{TiO}_2(110)$. The surface acid-base chemistry of H^+ and the carboxylate involves O anion and Ti cation sites. On $\text{TiO}_2(110)$, the proton is bound to 2-fold coordinated, bridging oxygen in the vicinity of TMA. However, for Ti_2O_3 and Ti_2O row models, what is used to be 2-fold coordinated bridging oxygen now forms rows. The site may no longer be active for H^+ bonding. Using combined STM and density functional theory (DFT) calculations, Lyubinetsky *et. al.* [30] reported that a physisorbed TMAA on $\text{TiO}_2(110)$ could serve as a mobile precursor to form a close-packed TMA overlayer. The calculated adsorption energy of the most stable molecularly-adsorbed TMAA via O – 5-fold coordinated Ti^{4+} and H-O_b bonding (Fig. 4.16c, middle & top) is only 0.19 eV lower than that of the dissociative bonding. Given that excess charges redistributes not only in the (1x2) strands but also on nearby 5-fold coordinated Ti^{4+} sites [64], it is plausible that the preference between the two configuration may even be smaller on (1x2) reconstructed $\text{TiO}_2(110)$.

In order to study the adsorption behavior of TMAA for higher coverages, we expose the surface shown in Fig 4.15b under a higher partial pressure (550 mTorr) of

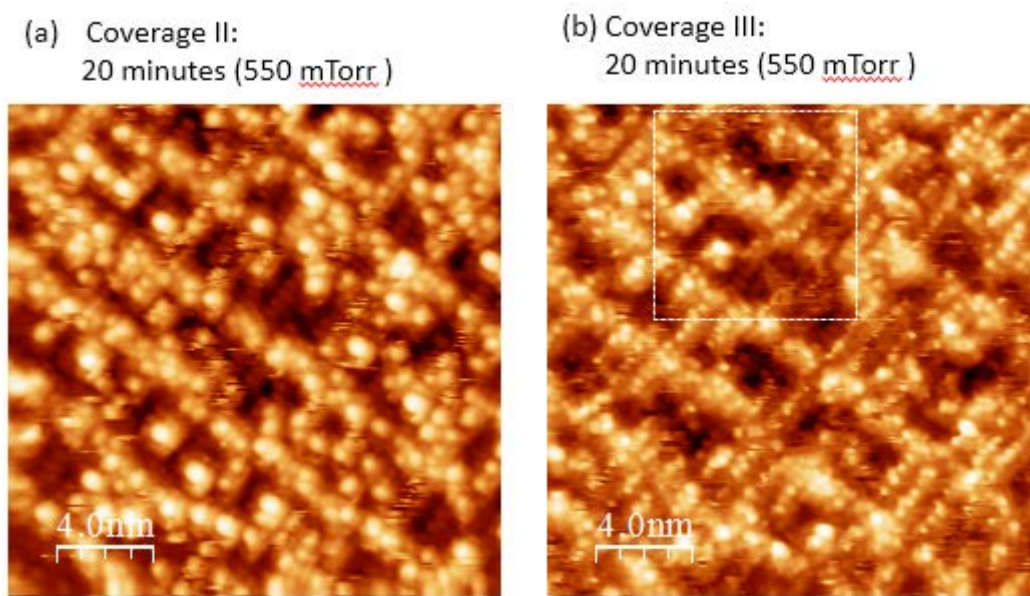


Figure 4.17 Two consecutive STM images are taken from the same area shown by Fig. 4.15b after additional TMAA exposures at room temperature. (a) the coverage II after additional exposure at 550 mTorr for 20 minutes, and (b) the coverage III after another 20 minute exposure at 550 mTorr.

TMAA environment at room temperature. Fig. 4.17 shows the same area after an additional exposure for 20 minutes (a, coverage II) and another sequential exposure for a same period (b, coverage III). After the additional exposure, the adsorption in troughs is supposed to be saturated through glimpses of trough areas and the coverage can be estimated roughly to 0.25 ML (see detail information in Ref. 62). And, the coverage of TMAA on crosslinks and on strands increase to 0.155 ML and 0.069 ML, respectively (Table 4.5). With another sequential coverage, the TMAA molecules on strands and crosslinks obscure the view of those in troughs. The final exposure to 550 mTorr for 20 minutes leads to only slight increase in TMAA on crosslinks (0.159 ML) as it is saturated with 95.6 % coverage. On

1x2 strands, the coverage is now increased to 0.105 ML, corresponding to 42% of the available 1x2 strand sites.

Table 4.5 Coverages of additional TMAA adsorptions on (1x2) TiO₂(110)

TMAA adsorption	Coverage II in ML (percentage)	Coverage after III in ML (percentage)
Strands	0.069 ML (27.6%)	0.105 ML (42%)
Crosslink	0.155 ML (93%)	0.159 ML (95.6%)

The experimental data further demonstrate which adsorption sites on (1x2) TiO₂(110) are preferred by TMAA molecules. After initial exposures (Table 4.4), the percentage of the occupied to the available sites is the largest for on-crosslinks, the second for in-troughs, and the least for on-strands. The difference in preference between on-crosslink and in-trough sites may be insignificant, but on-strand site is clearly least favored of the three. Only after the two sites are saturated and no longer available, a significant amount of TMAA molecules is observed to adsorb on strand sites (Table 4.5).

Closer-up views of TMAA on strands reveal similar traits observed on TMAA adsorbed in troughs. TMAA are lined up generally along [001] – along the strands (Fig. 4.18b). The nearest neighbor distance at a high coverage is estimated as 6 Å, approximately the same value observed for two adjacent TMAA in troughs as well as on (1x1) TiO₂(110). However, there is also considerably more disorder in adsorption on strands, compared to

that in troughs. Although many TMAA molecules appear right on the center of the strands, others clearly adsorb off-centered on strands (Fig. 4.18a).

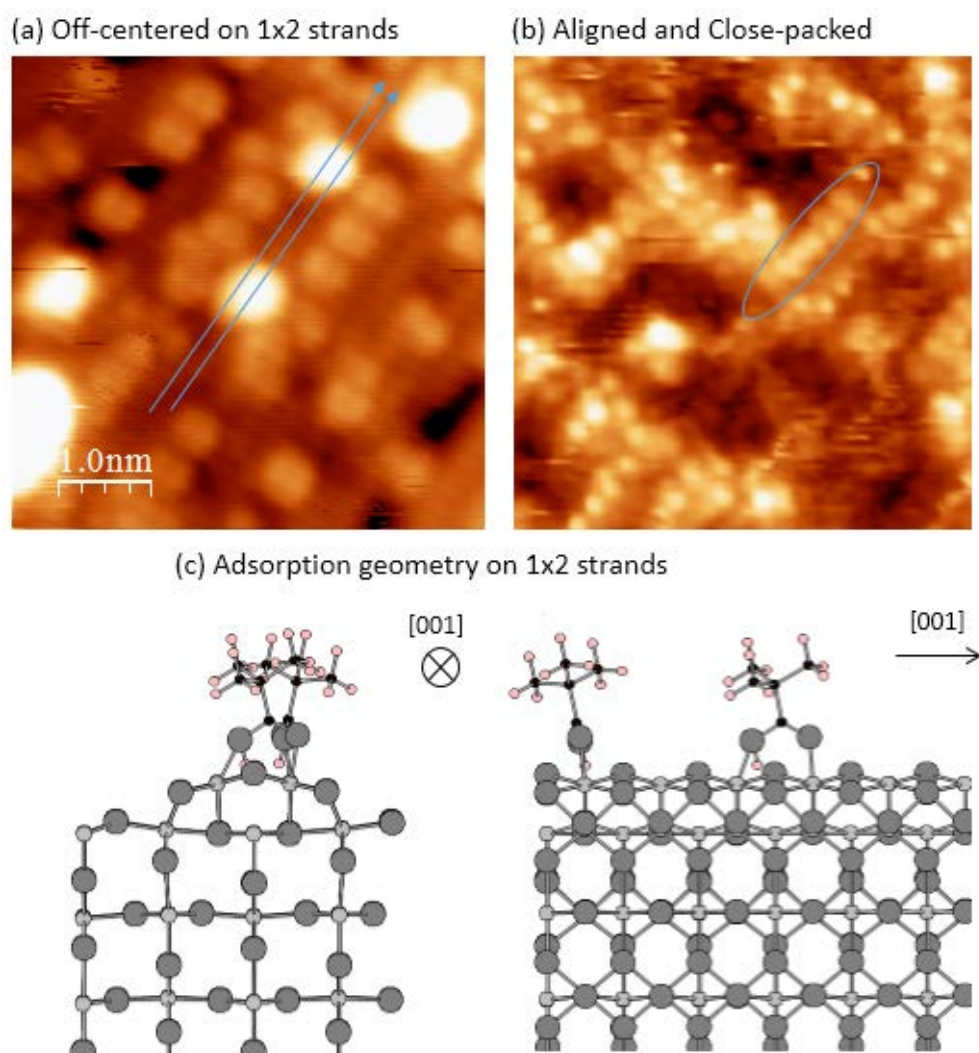


Figure 4.18 Close-up views of TMAA with (a) off-centered and (b) centered and forming a line on strands and (c) two possible adsorption geometry of TMAA molecules: one with bi-dentate configuration above two Ti cations along $[1 \bar{1} 0]$ and the other above two Ti cations along $[001]$ using the Ti_2O row model.

The two row models, Ti_2O_3 and Ti_2O , offer markedly different surface termination of the rows. Being terminated with 2-fold coordinated bridging oxygen, the Ti_2O_3 row structure has no exposed Ti sites (Fig. 1.6a). Assuming that TMAA similarly adsorbs with its carboxylic group down toward the row surface, the Ti_2O_3 row model poses a serious conflict with the STM observation. On the other hand, the Ti_2O row structure has double rows of Ti cations exposed and running along [001] (Fig. 1.6b). The Ti cations of the double rows are separated by 2.78 Å along [110] and 2.96 Å along [001] [13, 65]. Because both distances between two adjacent Ti cations are comparable to the distance between two oxygens of the carboxylic group in TMAA, two different bonding configurations are possible. With two oxygen atoms of TMAA bonded via two Ti cations along [110], the resulting TMAA is positioned approximately centered on the row structure (Fig. 4.18c). Two oxygen atoms of TMAA can be also bonded to two Ti cations along [001], analogous to TMAA adsorbed in troughs as well as on (1x1) $\text{TiO}_2(110)$. The resulting TMAA is off-centered on the row structure (Fig. 4.18c). In both configurations, either molecular or dissociative adsorption of TMAA is plausible. However, a significant number of TMAA on strands are observed to diffuse along the rows and desorb over a period of time under UHV. Therefore with the same reasoning as before for TMAA adsorbed in trough, it is proposed that TMAA adsorb on strands without dissociation.

CHAPTER FIVE

Conclusion

In this dissertation, rutile $\text{TiO}_2(110)$ with its well-known surface defects is studied for its structure and properties. An SPALEED study is performed for the structure of (1×1) $\text{TiO}_2(110)$ with modeling the optimizable slab layers up to four. The resultant structure reveals well-accepted relaxation features of the surface reported in other reports [2, 11, 13]. The relaxed positions of atoms point to the trend that the relaxation is strongest in the surface layer, where Ti-O bonds are severed. They eventually converge to bulk positions as the fourth slab layer is reached. In addition, the characteristic sequence of alternating contraction-elongation in Ti-O bonds is observed as the interlayer spacing is examined from the surface to bulk. Such sequences is understood as titanium cations displaced in the relatively rigid octahedral cages formed by oxygen atoms.

An *in situ* variable-temperature STM is used to study the catalytic property on partially reduced (1×1) $\text{TiO}_2(110)$. At low temperature, consecutive STM images from 75 K to 170 K successfully visualize the catalytic reaction: a diolate species, $-\text{OCH}_2\text{CH}_2\text{O}-$, is formed via coupling of one Ti-bound CH_2O and one of its product after adsorbing on V_O site: V_O -bound CH_2O . Detailed STM image shows the diolate is positioned off-centered to the O_b rows. It suggests the diolate binds on one side of Ti row and on the other side of O_b row as its oxygen replaces O_b . The study also indicates that the formation

of the diolate is a minor channel since it requires both Ti-bound CH_2O and V_O -bound CH_2O , whose mobility is limited, diffuse to the sites of vicinity. At room temperature, STM images reveal the diolate forms a stable coverage and becomes the dominate species on the surface. The diolate is suggested to explain the high temperature TPD desorption peak of C_2H_4 on the TiO_2 (110) with formaldehyde adsorption [25].

To investigate (1x2) reconstructed TiO_2 (110), SPALEED is performed with a reference structure based on Ti_2O added row. LT experimental data of fractional beams are best fitted to generate the optimized structure and the R-factor (R_p). In the resultant structure, dramatically contracted or elongated Ti-O bonds are observed. It suggest that the structure is unphysical and likely over-driven by the algorithm merely to minimize R_p . The value of R-factor 0.51 is similar to that reported by Ref. 18. Such a value indicates an indefinite correlation between the resultant structure and experimental data. By reviewing a recent modeling study of SPALEED [12], it is concluded that two optimizable layers used in this work are insufficient. To obtain a credible structure with Ti_2O added row, more optimizable layers are necessary, for instance, the layers containing another 25 inequivalent atoms. In order to fit with twice as many parameters, the extra energy ranges of experimental data (~ 1000 eV) are required to keep the standard of energy range per search freedom as 50 eV. For this purpose, improvement of experimental instrument is needed such as lower cryogenic temperature, electron gun with sharper focus *etc.*

To further investigate (1x2) reconstruction, a novel analysis using chemical probe, which successfully explained the STM image of (1x1) TiO_2 [29], is performed and it

gives a more explicit result. *In situ* room-temperature STM study identifies three adsorption sites of TMAA molecules on (1x2) cross-linked surfaces: on cross-links, in troughs, and on strands. Statistics show that they are preferred to adsorb on cross-link or in trough sites with comparable coverages while the adsorption on strand sites is less preferable. At low coverages, the TMAA molecules are mostly isolated in troughs. With increasing coverages, they start forming a close-packed “quasi-1D” chain along [001], separated by (1x2) strands. The observed adsorption of TMAA in troughs is consistent with both the Ti_2O_3 and the Ti_2O models but not with the Ti_3O_6 model due to narrow spacing. At higher coverages, TMAA molecules are adsorbed on strands both centered and off-centered configurations. The observed adsorption is consistent with the locations of the Ti cations on the Ti_2O model, but not consistent with the Ti_2O_3 model, which does not have the cationic sites exposed.

Experimentally, chemical probe study in this dissertation and the study of high resolution transmission microscopy by Shibata *et. al.*[19] support Ti_2O added row model. Theoretically, SPALEED calculations by M. Blanco-Ray *et. al.* [17, 18] and DFT calculations by Unal *et. al.* [64] support Ti_2O_3 added row model. Overall, the findings in the structural studies of (1x2) reconstructed TiO_2 are still contentious. For a deeper understanding, further researches using novel experimental and theoretical methods need to be performed.

APPENDICES

APPENDIX A

Grid Search Script for (1x1) TiO₂(110)

File – strsh

```
rm iv1 iv2 iv3 iv4 iv5 iv6 iv7 iv8 tleed.o gleed.o short.t prdir.d restart.d stru.txt strurf.txt search.s;
./mpt11.exe
for x in $(seq -w -0.3 0.15 00.3);
do for y in $(seq -w -0.3 0.15 00.3);
do for l in $(seq -w -0.3 0.15 00.3);
do for m in $(seq -w -0.3 0.15 00.3);
do for n in $(seq -w -0.3 0.15 00.3);
do (echo '14d'; echo '13a'; echo "${x}000 0.0000 0.0000 1"; echo '.'; echo 'wq')| ed tleed4.i;
(echo '15d'; echo '14a'; echo "${y}000 0.0000 0.0000 1"; echo '.'; echo 'wq')| ed tleed4.i;
(echo '16d'; echo '15a'; echo "${l}000 0.0000 0.0000 1"; echo '.'; echo 'wq')| ed tleed4.i;
(echo '17d'; echo '16a'; echo "${y}000 0.0000 0.0000 1"; echo '.'; echo 'wq')| ed tleed4.i;
(echo '18d'; echo '17a'; echo "${m}000 0.0000 0.0000 1"; echo '.'; echo 'wq')| ed tleed4.i;
(echo '19d'; echo '18a'; echo "${n}000 0.0000 0.0000 1"; echo '.'; echo 'wq')| ed tleed4.i;
./mpt21.exe
echo "${x} ${y} 0.0 ${l} ${m} ${n}" >> stru.txt;
echo 45 | ed search.s >> stru.txt;
echo 45 | ed search.s >> strurf.txt;
echo 46 | ed search.s >> strurf.txt;
rm iv1 iv2 iv3 iv4 iv5 iv6 iv7 iv8 gleed.o prdir.d restart.d search.s;
done;
done;
done;
done;

done
```

APPENDIX B

Input Files of SATLEED for (1x1) TiO₂(110)

File - tleed4.i

[illegible]

0.0000 0.0000 0.0000 1	DISP(1,I) I=1,3; LFLAG(1)
0.0000 0.0000 0.0000 1	DISP(1,I) I=1,3; LFLAG(1)
0.0000 0.0000 0.0000 1	DISP(1,I) I=1,3; LFLAG(1)
0.0000 0.0000 0.0000 1	DISP(1,I) I=1,3; LFLAG(1)
0.0000 0.0000 0.0000 1	DISP(1,I) I=1,3; LFLAG(1)
0.0000 0.0000 0.0000 1	DISP(1,I) I=1,3; LFLAG(1)
0.05 1	
2 0 0	MFLAG,NGRID,NIV
900	ITMAX
1.0000 0.5000 2.0000	ALPHA,BETA,GAMMA
0.001 0.0005	FTOL1,FTOL2

File - tleed5.i

TiO₂(110) clean

2	IDEG
30	NPSI
0.5000 0.6400	FR ASE
0.002	TST
0.00 0.00	THETA FI
6.39 -5.00	VV VI
8	LMAX
5	NEL
1 1 1 1 1	IT
300.0000 15.9994 1.0000 1.0000 0.0035	
300.0000 47.8671 1.0000 1.0000 0.0004	
300.0000 15.9994 1.0000 1.0000 0.0035	
450.0000 47.8671 1.0000 1.0000 0.0002	
450.0000 15.9994 1.0000 1.0000 0.0016	
140.0000	TI
2.0000	
-2.3292 2.0194 0.3779 0.0388 0.0034 0.0002 0.0000 0.0000 0.0000	
-2.0272 2.0754-0.5717 0.1975 0.0130 0.0008 0.0000 0.0000 0.0000	
-2.3292 2.0194 0.3779 0.0388 0.0034 0.0002 0.0000 0.0000 0.0000	
-2.0272 2.0754-0.5717 0.1975 0.0130 0.0008 0.0000 0.0000 0.0000	
-2.3292 2.0194 0.3779 0.0388 0.0034 0.0002 0.0000 0.0000 0.0000	

2.3448
 -2.4254 1.9826 0.4775 0.0600 0.0062 0.0005 0.0000 0.0000 0.0000
 -2.1312 2.0006-0.5870 0.3221 0.0239 0.0018 0.0001 0.0000 0.0000
 -2.4254 1.9826 0.4775 0.0600 0.0062 0.0005 0.0000 0.0000 0.0000
 -2.1312 2.0006-0.5870 0.3221 0.0239 0.0018 0.0001 0.0000 0.0000
 -2.4254 1.9826 0.4775 0.0600 0.0062 0.0005 0.0000 0.0000 0.0000
 2.6897
 -2.5069 1.9547 0.5624 0.0857 0.0103 0.0009 0.0001 0.0000 0.0000
 -2.2226 1.9385-0.5891 0.4756 0.0401 0.0034 0.0002 0.0000 0.0000
 -2.5069 1.9547 0.5624 0.0857 0.0103 0.0009 0.0001 0.0000 0.0000
 -2.2226 1.9385-0.5891 0.4756 0.0401 0.0034 0.0002 0.0000 0.0000
 -2.5069 1.9547 0.5624 0.0857 0.0103 0.0009 0.0001 0.0000 0.0000
 3.0345
 -2.5775 1.9330 0.6301 0.1152 0.0157 0.0016 0.0001 0.0000 0.0000
 -2.3054 1.8850-0.5806 0.6402 0.0625 0.0060 0.0005 0.0000 0.0000
 -2.5775 1.9330 0.6301 0.1152 0.0157 0.0016 0.0001 0.0000 0.0000
 -2.3054 1.8850-0.5806 0.6402 0.0625 0.0060 0.0005 0.0000 0.0000
 -2.5775 1.9330 0.6301 0.1152 0.0157 0.0016 0.0001 0.0000 0.0000
 3.3793
 -2.6399 1.9151 0.6817 0.1473 0.0227 0.0027 0.0002 0.0000 0.0000
 -2.3822 1.8371-0.5649 0.7940 0.0918 0.0098 0.0009 0.0001 0.0000
 -2.6399 1.9151 0.6817 0.1473 0.0227 0.0027 0.0002 0.0000 0.0000
 -2.3822 1.8371-0.5649 0.7940 0.0918 0.0098 0.0009 0.0001 0.0000
 -2.6399 1.9151 0.6817 0.1473 0.0227 0.0027 0.0002 0.0000 0.0000
 3.7241
 -2.6961 1.8993 0.7202 0.1809 0.0312 0.0041 0.0004 0.0000 0.0000
 -2.4547 1.7925-0.5457 0.9217 0.1283 0.0151 0.0015 0.0001 0.0000
 -2.6961 1.8993 0.7202 0.1809 0.0312 0.0041 0.0004 0.0000 0.0000
 -2.4547 1.7925-0.5457 0.9217 0.1283 0.0151 0.0015 0.0001 0.0000
 -2.6961 1.8993 0.7202 0.1809 0.0312 0.0041 0.0004 0.0000 0.0000
 4.0690
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 -2.7475 1.8845 0.7487 0.2147 0.0413 0.0060 0.0007 0.0001 0.0000
 -2.5242 1.7495-0.5264 1.0194 0.1721 0.0221 0.0024 0.0002 0.0000
 -2.7475 1.8845 0.7487 0.2147 0.0413 0.0060 0.0007 0.0001 0.0000
 4.4138
 -2.7952 1.8700 0.7698 0.2476 0.0529 0.0084 0.0010 0.0001 0.0000
 -2.5912 1.7073-0.5096 1.0906 0.2223 0.0313 0.0037 0.0003 0.0000
 -2.7952 1.8700 0.7698 0.2476 0.0529 0.0084 0.0010 0.0001 0.0000
 -2.5912 1.7073-0.5096 1.0906 0.2223 0.0313 0.0037 0.0003 0.0000

-2.7952 1.8700 0.7698 0.2476 0.0529 0.0084 0.0010 0.0001 0.0000
 4.7586
 -2.8400 1.8554 0.7858 0.2787 0.0658 0.0113 0.0015 0.0001 0.0000
 -2.6562 1.6652-0.4970 1.1411 0.2777 0.0427 0.0054 0.0005 0.0000
 -2.8400 1.8554 0.7858 0.2787 0.0658 0.0113 0.0015 0.0001 0.0000
 -2.6562 1.6652-0.4970 1.1411 0.2777 0.0427 0.0054 0.0005 0.0000
 -2.8400 1.8554 0.7858 0.2787 0.0658 0.0113 0.0015 0.0001 0.0000
 5.1034
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 -2.7194 1.6230-0.4893 1.1767 0.3363 0.0566 0.0077 0.0008 0.0001
 -2.8825 1.8404 0.7983 0.3074 0.0798 0.0149 0.0021 0.0002 0.0000
 -2.7194 1.6230-0.4893 1.1767 0.3363 0.0566 0.0077 0.0008 0.0001
 -2.8825 1.8404 0.7983 0.3074 0.0798 0.0149 0.0021 0.0002 0.0000
 5.4483
 -2.9229 1.8251 0.8086 0.3333 0.0947 0.0192 0.0029 0.0003 0.0000
 -2.7809 1.5807-0.4865 1.2020 0.3959 0.0731 0.0107 0.0013 0.0001
 -2.9229 1.8251 0.8086 0.3333 0.0947 0.0192 0.0029 0.0003 0.0000
 -2.7809 1.5807-0.4865 1.2020 0.3959 0.0731 0.0107 0.0013 0.0001
 -2.9229 1.8251 0.8086 0.3333 0.0947 0.0192 0.0029 0.0003 0.0000
 5.7931
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 6.1379
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 -2.8987 1.4963-0.4937 1.2350 0.5092 0.1140 0.0191 0.0026 0.0003
 -2.9990 1.7941 0.8256 0.3764 0.1262 0.0296 0.0052 0.0007 0.0001
 -2.8987 1.4963-0.4937 1.2350 0.5092 0.1140 0.0191 0.0026 0.0003
 -2.9990 1.7941 0.8256 0.3764 0.1262 0.0296 0.0052 0.0007 0.0001
 6.4828
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 -2.9549 1.4546-0.5023 1.2471 0.5594 0.1382 0.0246 0.0035 0.0004
 -3.0349 1.7786 0.8332 0.3938 0.1423 0.0358 0.0067 0.0010 0.0001
 -2.9549 1.4546-0.5023 1.2471 0.5594 0.1382 0.0246 0.0035 0.0004
 -3.0349 1.7786 0.8332 0.3938 0.1423 0.0358 0.0067 0.0010 0.0001
 6.8276
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 -3.0695 1.7633 0.8406 0.4088 0.1581 0.0426 0.0085 0.0013 0.0002

-3.0094 1.4135-0.5132 1.2583 0.6041 0.1647 0.0313 0.0047 0.0006
 -3.0695 1.7633 0.8406 0.4088 0.1581 0.0426 0.0085 0.0013 0.0002
 7.1724
 -3.1028 1.7484 0.8478 0.4217 0.1735 0.0499 0.0106 0.0017 0.0002
 -3.0621 1.3731-0.5257 1.2694 0.6429 0.1929 0.0390 0.0062 0.0008
 -3.1028 1.7484 0.8478 0.4217 0.1735 0.0499 0.0106 0.0017 0.0002
 -3.0621 1.3731-0.5257 1.2694 0.6429 0.1929 0.0390 0.0062 0.0008
 -3.1028 1.7484 0.8478 0.4217 0.1735 0.0499 0.0106 0.0017 0.0002
 7.5172
 -3.1350 1.7340 0.8548 0.4328 0.1884 0.0578 0.0129 0.0022 0.0003
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 -3.1350 1.7340 0.8548 0.4328 0.1884 0.0578 0.0129 0.0022 0.0003
 -3.1129 1.3337-0.5392 1.2810 0.6759 0.2225 0.0480 0.0081 0.0011
 -3.1350 1.7340 0.8548 0.4328 0.1884 0.0578 0.0129 0.0022 0.0003
 7.8621
 -3.1660 1.7202 0.8616 0.4425 0.2024 0.0660 0.0156 0.0028 0.0004
 -3.1619 1.2955-0.5531 1.2934 0.7036 0.2529 0.0581 0.0103 0.0015
 -3.1660 1.7202 0.8616 0.4425 0.2024 0.0660 0.0156 0.0028 0.0004
 -3.1619 1.2955-0.5531 1.2934 0.7036 0.2529 0.0581 0.0103 0.0015
 -3.1660 1.7202 0.8616 0.4425 0.2024 0.0660 0.0156 0.0028 0.0004
 8.2069
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 -3.2089 1.2584-0.5671 1.3069 0.7266 0.2836 0.0695 0.0130 0.0019
 -3.1958 1.7071 0.8682 0.4509 0.2157 0.0746 0.0187 0.0036 0.0005
 -3.2089 1.2584-0.5671 1.3069 0.7266 0.2836 0.0695 0.0130 0.0019
 -3.1958 1.7071 0.8682 0.4509 0.2157 0.0746 0.0187 0.0036 0.0005
 8.5517
 -3.2244 1.6946 0.8744 0.4585 0.2279 0.0834 0.0220 0.0044 0.0007
 -3.2541 1.2227-0.5806 1.3211 0.7456 0.3140 0.0821 0.0161 0.0025
 -3.2244 1.6946 0.8744 0.4585 0.2279 0.0834 0.0220 0.0044 0.0007
 -3.2541 1.2227-0.5806 1.3211 0.7456 0.3140 0.0821 0.0161 0.0025
 -3.2244 1.6946 0.8744 0.4585 0.2279 0.0834 0.0220 0.0044 0.0007
 8.8966
 -3.2520 1.6828 0.8801 0.4653 0.2393 0.0924 0.0257 0.0054 0.0009
 -3.2974 1.1884-0.5935 1.3361 0.7612 0.3436 0.0959 0.0198 0.0032
 -3.2520 1.6828 0.8801 0.4653 0.2393 0.0924 0.0257 0.0054 0.0009
 -3.2974 1.1884-0.5935 1.3361 0.7612 0.3436 0.0959 0.0198 0.0032
 -3.2520 1.6828 0.8801 0.4653 0.2393 0.0924 0.0257 0.0054 0.0009
 9.2414
 -3.2784 1.6717 0.8854 0.4717 0.2496 0.1015 0.0297 0.0065 0.0011
 -3.3388 1.1556-0.6056 1.3515 0.7741 0.3719 0.1107 0.0240 0.0041

-3.2784 1.6717 0.8854 0.4717 0.2496 0.1015 0.0297 0.0065 0.0011
 -3.3388 1.1556-0.6056 1.3515 0.7741 0.3719 0.1107 0.0240 0.0041
 -3.2784 1.6717 0.8854 0.4717 0.2496 0.1015 0.0297 0.0065 0.0011
 9.5862
 -3.3038 1.6613 0.8901 0.4777 0.2591 0.1105 0.0340 0.0078 0.0014
 -3.3785 1.1243-0.6167 1.3670 0.7849 0.3987 0.1266 0.0287 0.0051
 -3.3038 1.6613 0.8901 0.4777 0.2591 0.1105 0.0340 0.0078 0.0014
 -3.3785 1.1243-0.6167 1.3670 0.7849 0.3987 0.1266 0.0287 0.0051
 -3.3038 1.6613 0.8901 0.4777 0.2591 0.1105 0.0340 0.0078 0.0014
 9.9310
 -3.3282 1.6515 0.8942 0.4834 0.2676 0.1194 0.0385 0.0093 0.0017
 -3.4164 1.0944-0.6267 1.3823 0.7942 0.4235 0.1433 0.0341 0.0064
 -3.3282 1.6515 0.8942 0.4834 0.2676 0.1194 0.0385 0.0093 0.0017
 -3.4164 1.0944-0.6267 1.3823 0.7942 0.4235 0.1433 0.0341 0.0064
 -3.3282 1.6515 0.8942 0.4834 0.2676 0.1194 0.0385 0.0093 0.0017
 10.2759
 -3.3516 1.6423 0.8976 0.4890 0.2754 0.1282 0.0434 0.0109 0.0021
 -3.4526 1.0661-0.6357 1.3970 0.8023 0.4463 0.1607 0.0401 0.0078
 -3.3516 1.6423 0.8976 0.4890 0.2754 0.1282 0.0434 0.0109 0.0021
 -3.4526 1.0661-0.6357 1.3970 0.8023 0.4463 0.1607 0.0401 0.0078
 -3.3516 1.6423 0.8976 0.4890 0.2754 0.1282 0.0434 0.0109 0.0021
 10.6207
 -3.3740 1.6336 0.9006 0.4945 0.2824 0.1367 0.0484 0.0127 0.0026
 -3.4872 1.0392-0.6436 1.4109 0.8097 0.4669 0.1787 0.0468 0.0095
 -3.3740 1.6336 0.9006 0.4945 0.2824 0.1367 0.0484 0.0127 0.0026
 -3.4872 1.0392-0.6436 1.4109 0.8097 0.4669 0.1787 0.0468 0.0095
 -3.3740 1.6336 0.9006 0.4945 0.2824 0.1367 0.0484 0.0127 0.0026
 10.9655
 -3.3956 1.6254 0.9029 0.4999 0.2887 0.1449 0.0536 0.0147 0.0031
 -3.5203 1.0136-0.6505 1.4237 0.8167 0.4854 0.1970 0.0541 0.0114
 -3.3956 1.6254 0.9029 0.4999 0.2887 0.1449 0.0536 0.0147 0.0031
 -3.5203 1.0136-0.6505 1.4237 0.8167 0.4854 0.1970 0.0541 0.0114
 -3.3956 1.6254 0.9029 0.4999 0.2887 0.1449 0.0536 0.0147 0.0031
 11.3103
 -3.4163 1.6176 0.9047 0.5052 0.2944 0.1528 0.0590 0.0169 0.0037
 -3.5519 0.9894-0.6564 1.4353 0.8235 0.5019 0.2155 0.0621 0.0136
 -3.4163 1.6176 0.9047 0.5052 0.2944 0.1528 0.0590 0.0169 0.0037
 -3.5519 0.9894-0.6564 1.4353 0.8235 0.5019 0.2155 0.0621 0.0136
 -3.4163 1.6176 0.9047 0.5052 0.2944 0.1528 0.0590 0.0169 0.0037
 11.6552
 -3.4362 1.6101 0.9060 0.5106 0.2997 0.1603 0.0646 0.0192 0.0044

-3.5821 0.9665-0.6616 1.4456 0.8305 0.5164 0.2339 0.0707 0.0161
 -3.4362 1.6101 0.9060 0.5106 0.2997 0.1603 0.0646 0.0192 0.0044
 -3.5821 0.9665-0.6616 1.4456 0.8305 0.5164 0.2339 0.0707 0.0161
 -3.4362 1.6101 0.9060 0.5106 0.2997 0.1603 0.0646 0.0192 0.0044
 12.0000
 -3.4554 1.6029 0.9069 0.5159 0.3045 0.1673 0.0702 0.0218 0.0052
 -3.6111 0.9447-0.6661 1.4545 0.8376 0.5291 0.2521 0.0799 0.0189
 -3.4554 1.6029 0.9069 0.5159 0.3045 0.1673 0.0702 0.0218 0.0052
 -3.6111 0.9447-0.6661 1.4545 0.8376 0.5291 0.2521 0.0799 0.0189
 -3.4554 1.6029 0.9069 0.5159 0.3045 0.1673 0.0702 0.0218 0.0052
 6.4960 0.0000 ARA1 (SUBSTRATE LATTICE VECTORS)
 0.0000 2.9580 ARA2
 6.4960 0.0000 ARB1 (OVERLAYER LATTICE VECTORS)
 0.0000 2.9580 ARB2
 1 IVECT (NUMBER OF INTERLAYER
 VECTORS)
 1.2650000 0.0000000 0.0000000 ASA(1,J),J=1,3
 3 2 3 NST1,NST1EFF,NTENS
 13 12 12 NLAY(i),i=1,NST1
 0 IFLAG
 5 2 2
 1 3 2 3 2 5 5 5 5 4 4 5 5
 5 4 5 4 5 5 5 5 4 4 5 5
 5 4 5 4 5 5 5 5 4 4 5 5
 0.0000 0.0000 0.0000
 1.1047 -2.1266 1.4790
 1.1150 0.0000 1.4790
 1.1047 2.1266 1.4790
 1.5406 3.2480 0.0000
 2.6167 0.0000 0.0000
 3.3123 3.2480 0.0000
 4.4689 -1.2954 1.4790
 4.4689 1.2954 1.4790
 4.7085 3.2480 1.4790
 4.4508 0.0000 0.0000
 5.8657 3.2480 0.0000
 6.6205 0.0000 0.0000
 1.2536 0.0000 0.0000 asb
 0.50 0.00 -5.00 FRCL(1),VCL(1),VICL(1)
 7.8741 -1.9835 1.4790 O(2)
 7.8741 0.0000 1.4790 Ti(1)

7.8741	1.9835	1.4790	O(2)
7.8741	3.2480	0.0000	Ti(2)
9.1391	0.0000	0.0000	O(3)
9.8571	3.2480	0.0000	O(4)
11.1221	-1.2650	1.4790	O(5)
11.1221	1.2650	1.4790	O(5)
11.1721	3.2480	1.4790	Ti(3)
11.1721	0.0000	0.0000	Ti(4)
12.3871	3.2480	0.0000	O(6)
13.0781	0.0000	0.0000	O
1.3650	0.0000	0.0000	asb
0.50	0.00	-5.00	FRCL(1),VCL(1),VICL(1)
14.4431	-1.9835	1.4790	O(2)
14.4431	0.0000	1.4790	Ti(1)
14.4431	1.9835	1.4790	O(2)
14.4431	3.2480	0.0000	Ti(2)
15.7081	0.0000	0.0000	O(3)
16.4261	3.2480	0.0000	O(4)
17.6911	-1.2650	1.4790	O(5)
17.6911	1.2650	1.4790	O(5)
17.6911	3.2480	1.4790	Ti(3)
17.6911	0.0000	0.0000	Ti(4)
18.9561	3.2480	0.0000	O(6)
20.2211	0.0000	0.0000	O
1.2650	0.0000	0.0000	asb
0.50	0.00	-5.00	FRCL(1),VCL(1),VICL(1)
50.00	300.00	2.00	EI EF DE

APPENDIX C

Input Files of STALEED for (1x2) TiO₂(110)

File - TLEED4.i

0 0 0	IPR	ISTART	LRFLAG
9 9 0.05 0.5	NSYM	NSYMS	ASTEP VSTEP
11 1 4 8	NT0	NSET	LSMAX LLCUT
11	NINSET		
1.0000 0.0000			
3.0000 0.0000			
5.0000 0.0000			
3.0000 1.0000			
1.0000 1.0000			
5.0000 1.0000			
1.0000 2.0000			
3.0000 2.0000			
7.0000 0.0000			
5.0000 2.0000			
7.0000 1.0000			
3	NDIM		
0.0000 0.0000 0.0000 1	DISP(1,I)	I=1,3;	LFLAG(1)
0.0000 0.0000 0.0000 1	DISP(1,I)	I=1,3;	LFLAG(1)
0.0000 0.0000 0.0000 1	DISP(1,I)	I=1,3;	LFLAG(1)
0.0000 0.0000 0.0000 1	DISP(1,I)	I=1,3;	LFLAG(1)
0.0000 0.0000 0.0000 1	DISP(1,I)	I=1,3;	LFLAG(1)
0.0000 0.0000 0.0000 1	DISP(1,I)	I=1,3;	LFLAG(1)
0.0000 0.0000 0.0000 1	DISP(1,I)	I=1,3;	LFLAG(1)
0.0000 0.0000 0.0000 1	DISP(1,I)	I=1,3;	LFLAG(1)
0.0000 0.0000 0.0000 1	DISP(1,I)	I=1,3;	LFLAG(1)
0.0000 0.0000 0.0000 1	DISP(1,I)	I=1,3;	LFLAG(1)
0.0000 0.0000 0.0000 1	DISP(1,I)	I=1,3;	LFLAG(1)
0.0000 0.0000 0.0000 1	DISP(1,I)	I=1,3;	LFLAG(1)
0.0000 0.0000 0.0000 1	DISP(1,I)	I=1,3;	LFLAG(1)
0.0000 0.0000 0.0000 1	DISP(1,I)	I=1,3;	LFLAG(1)
0.0000 0.0000 0.0000 1	DISP(1,I)	I=1,3;	LFLAG(1)
0.0000 0.0000 0.0000 1	DISP(1,I)	I=1,3;	LFLAG(1)
0.0000 0.0000 0.0000 1	DISP(1,I)	I=1,3;	LFLAG(1)

0.0000 0.0000 0.0000 1	DISP(1,I) I=1,3; LFLAG(1)
0.0000 0.0000 0.0000 1	DISP(1,I) I=1,3; LFLAG(1)
0.0000 0.0000 0.0000 1	DISP(1,I) I=1,3; LFLAG(1)
0.0000 0.0000 0.0000 1	DISP(1,I) I=1,3; LFLAG(1)
0.0000 0.0000 0.0000 1	DISP(1,I) I=1,3; LFLAG(1)
0.0000 0.0000 0.0000 1	DISP(1,I) I=1,3; LFLAG(1)
0.0000 0.0000 0.0000 1	DISP(1,I) I=1,3; LFLAG(1)
0.0000 0.0000 0.0000 1	DISP(1,I) I=1,3; LFLAG(1)
0.0000 0.0000 0.0000 1	DISP(1,I) I=1,3; LFLAG(1)
0.0000 0.0000 0.0000 1	DISP(1,I) I=1,3; LFLAG(1)
0.0000 0.0000 0.0000 1	DISP(1,I) I=1,3; LFLAG(1)
0.0000 0.0000 0.0000 1	DISP(1,I) I=1,3; LFLAG(1)
0.0000 0.0000 0.0000 1	DISP(1,I) I=1,3; LFLAG(1)
0.0500 1	
2 0 0	MFLAG,NGRID,NIV
900	ITMAX
1.0000 0.5000 2.0000	ALPHA,BETA,GAMMA
0.001 0.0005	FTOL1,FTOL2

File – tleed5.i

TiO₂(110) 1x2 clean

2	IDEG
74	NPSI
0.5000 0.6400	FR ASE ase may be searched
0.002	TST
0.00 0.00	THETA FI
6.30 -5.00	VV VI
8	LMAX
5	NEL
1 1 1 1 1	IT
300.0000 15.9994 0.1200 0.1200 0.0016	
370.0000 47.8671 0.3000 0.3000 0.0002	
300.0000 15.9994 0.1200 0.1200 0.0016	
370.0000 47.8671 0.1200 0.1200 0.0002	
300.0000 15.9994 0.1200 0.1200 0.0016	
190.0000	TI
0.5880	Oxygen - Titanium

1.4080-1.1681 0.0162 0.0005 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
 -1.3542-0.6081 0.4140 0.0044 0.0001 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
 1.4080-1.1681 0.0162 0.0005 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
 -1.3542-0.6081 0.4140 0.0044 0.0001 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
 1.4080-1.1681 0.0162 0.0005 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
 0.8820
 1.1769-1.1433 0.0411 0.0018 0.0001 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
 -1.5941-0.7946 1.6416 0.0163 0.0008 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
 1.1769-1.1433 0.0411 0.0018 0.0001 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
 -1.5941-0.7946 1.6416 0.0163 0.0008 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
 1.1769-1.1433 0.0411 0.0018 0.0001 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
 1.1760
 1.0010-1.1855 0.0754 0.0042 0.0002 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
 -1.7804-0.9406 2.1086 0.0397 0.0026 0.0001 0.0000 0.0000 0.0000 0.0000 0.0000
 1.0010-1.1855 0.0754 0.0042 0.0002 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
 -1.7804-0.9406 2.1086 0.0397 0.0026 0.0001 0.0000 0.0000 0.0000 0.0000 0.0000
 1.0010-1.1855 0.0754 0.0042 0.0002 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
 1.4700
 0.8675-1.2230 0.1254 0.0087 0.0005 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
 -1.9321-1.0560 2.2356 0.0760 0.0059 0.0004 0.0000 0.0000 0.0000 0.0000 0.0000
 0.8675-1.2230 0.1254 0.0087 0.0005 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
 -1.9321-1.0560 2.2356 0.0760 0.0059 0.0004 0.0000 0.0000 0.0000 0.0000 0.0000
 0.8675-1.2230 0.1254 0.0087 0.0005 0.0000 0.0000 0.0000 0.0000 0.0000 0.0000
 1.7641
 0.7656-1.2488 0.1961 0.0167 0.0012 0.0001 0.0000 0.0000 0.0000 0.0000 0.0000
 -2.0517-1.1426 2.2932 0.1306 0.0116 0.0009 0.0001 0.0000 0.0000 0.0000 0.0000
 0.7656-1.2488 0.1961 0.0167 0.0012 0.0001 0.0000 0.0000 0.0000 0.0000 0.0000
 -2.0517-1.1426 2.2932 0.1306 0.0116 0.0009 0.0001 0.0000 0.0000 0.0000 0.0000
 0.7656-1.2488 0.1961 0.0167 0.0012 0.0001 0.0000 0.0000 0.0000 0.0000 0.0000
 2.0581
 0.6751-1.2780 0.2674 0.0265 0.0023 0.0001 0.0000 0.0000 0.0000 0.0000 0.0000
 -2.1561-1.2157 2.3179 0.2021 0.0206 0.0019 0.0001 0.0000 0.0000 0.0000 0.0000
 0.6751-1.2780 0.2674 0.0265 0.0023 0.0001 0.0000 0.0000 0.0000 0.0000 0.0000
 -2.1561-1.2157 2.3179 0.2021 0.0206 0.0019 0.0001 0.0000 0.0000 0.0000 0.0000
 0.6751-1.2780 0.2674 0.0265 0.0023 0.0001 0.0000 0.0000 0.0000 0.0000 0.0000
 2.3521
 0.5957-1.3044 0.3353 0.0383 0.0037 0.0003 0.0000 0.0000 0.0000 0.0000 0.0000
 -2.2498-1.2799 2.3335 0.2875 0.0333 0.0036 0.0003 0.0000 0.0000 0.0000 0.0000
 0.5957-1.3044 0.3353 0.0383 0.0037 0.0003 0.0000 0.0000 0.0000 0.0000 0.0000
 -2.2498-1.2799 2.3335 0.2875 0.0333 0.0036 0.0003 0.0000 0.0000 0.0000 0.0000
 0.5957-1.3044 0.3353 0.0383 0.0037 0.0003 0.0000 0.0000 0.0000 0.0000 0.0000

2.6461
 0.5246-1.3284 0.3969 0.0519 0.0057 0.0005 0.0000 0.0000 0.0000 0.0000 0.0000
 -2.3365-1.3382 2.3468 0.3804 0.0497 0.0061 0.0006 0.0000 0.0000 0.0000 0.0000
 0.5246-1.3284 0.3969 0.0519 0.0057 0.0005 0.0000 0.0000 0.0000 0.0000 0.0000
 -2.3365-1.3382 2.3468 0.3804 0.0497 0.0061 0.0006 0.0000 0.0000 0.0000 0.0000
 0.5246-1.3284 0.3969 0.0519 0.0057 0.0005 0.0000 0.0000 0.0000 0.0000 0.0000
 2.9401
 0.4604-1.3498 0.4521 0.0672 0.0082 0.0008 0.0001 0.0000 0.0000 0.0000 0.0000
 -2.4177-1.3927 2.3593 0.4740 0.0700 0.0095 0.0010 0.0001 0.0000 0.0000 0.0000
 0.4604-1.3498 0.4521 0.0672 0.0082 0.0008 0.0001 0.0000 0.0000 0.0000 0.0000
 -2.4177-1.3927 2.3593 0.4740 0.0700 0.0095 0.0010 0.0001 0.0000 0.0000 0.0000
 0.4604-1.3498 0.4521 0.0672 0.0082 0.0008 0.0001 0.0000 0.0000 0.0000 0.0000
 3.2341
 0.4030-1.3678 0.5013 0.0843 0.0113 0.0012 0.0001 0.0000 0.0000 0.0000 0.0000
 -2.4933-1.4430 2.3723 0.5644 0.0943 0.0141 0.0017 0.0002 0.0000 0.0000 0.0000
 0.4030-1.3678 0.5013 0.0843 0.0113 0.0012 0.0001 0.0000 0.0000 0.0000 0.0000
 -2.4933-1.4430 2.3723 0.5644 0.0943 0.0141 0.0017 0.0002 0.0000 0.0000 0.0000
 0.4030-1.3678 0.5013 0.0843 0.0113 0.0012 0.0001 0.0000 0.0000 0.0000 0.0000
 3.5281
 0.3516-1.3826 0.5452 0.1032 0.0152 0.0017 0.0002 0.0000 0.0000 0.0000 0.0000
 -2.5637-1.4897 2.3857 0.6483 0.1229 0.0202 0.0027 0.0003 0.0000 0.0000 0.0000
 0.3516-1.3826 0.5452 0.1032 0.0152 0.0017 0.0002 0.0000 0.0000 0.0000 0.0000
 -2.5637-1.4897 2.3857 0.6483 0.1229 0.0202 0.0027 0.0003 0.0000 0.0000 0.0000
 0.3516-1.3826 0.5452 0.1032 0.0152 0.0017 0.0002 0.0000 0.0000 0.0000 0.0000
 3.8221
 0.3038-1.3964 0.5811 0.1227 0.0197 0.0025 0.0002 0.0000 0.0000 0.0000 0.0000
 -2.6314-1.5355 2.3961 0.7203 0.1539 0.0277 0.0041 0.0005 0.0000 0.0000 0.0000
 0.3038-1.3964 0.5811 0.1227 0.0197 0.0025 0.0002 0.0000 0.0000 0.0000 0.0000
 -2.6314-1.5355 2.3961 0.7203 0.1539 0.0277 0.0041 0.0005 0.0000 0.0000 0.0000
 0.3038-1.3964 0.5811 0.1227 0.0197 0.0025 0.0002 0.0000 0.0000 0.0000 0.0000
 4.1161
 0.2588-1.4101 0.6100 0.1418 0.0246 0.0033 0.0003 0.0000 0.0000 0.0000 0.0000
 -2.6967-1.5807 2.4028 0.7804 0.1861 0.0363 0.0058 0.0007 0.0001 0.0000 0.0000
 0.2588-1.4101 0.6100 0.1418 0.0246 0.0033 0.0003 0.0000 0.0000 0.0000 0.0000
 -2.6967-1.5807 2.4028 0.7804 0.1861 0.0363 0.0058 0.0007 0.0001 0.0000 0.0000
 0.2588-1.4101 0.6100 0.1418 0.0246 0.0033 0.0003 0.0000 0.0000 0.0000 0.0000
 4.4101
 0.2166-1.4231 0.6336 0.1607 0.0300 0.0043 0.0005 0.0000 0.0000 0.0000 0.0000
 -2.7592-1.6248 2.4069 0.8308 0.2191 0.0462 0.0079 0.0011 0.0001 0.0000 0.0000
 0.2166-1.4231 0.6336 0.1607 0.0300 0.0043 0.0005 0.0000 0.0000 0.0000 0.0000
 -2.7592-1.6248 2.4069 0.8308 0.2191 0.0462 0.0079 0.0011 0.0001 0.0000 0.0000

0.2166-1.4231 0.6336 0.1607 0.0300 0.0043 0.0005 0.0000 0.0000 0.0000 0.0000
 4.7042
 0.1776-1.4347 0.6538 0.1802 0.0362 0.0056 0.0007 0.0001 0.0000 0.0000 0.0000
 -2.8182-1.6666 2.4096 0.8746 0.2535 0.0579 0.0107 0.0016 0.0002 0.0000 0.0000
 0.1776-1.4347 0.6538 0.1802 0.0362 0.0056 0.0007 0.0001 0.0000 0.0000 0.0000
 -2.8182-1.6666 2.4096 0.8746 0.2535 0.0579 0.0107 0.0016 0.0002 0.0000 0.0000
 0.1776-1.4347 0.6538 0.1802 0.0362 0.0056 0.0007 0.0001 0.0000 0.0000 0.0000
 4.9982
 0.1417-1.4448 0.6718 0.2002 0.0433 0.0072 0.0009 0.0001 0.0000 0.0000 0.0000
 -2.8736-1.7061 2.4117 0.9134 0.2888 0.0715 0.0143 0.0023 0.0003 0.0000 0.0000
 0.1417-1.4448 0.6718 0.2002 0.0433 0.0072 0.0009 0.0001 0.0000 0.0000 0.0000
 -2.8736-1.7061 2.4117 0.9134 0.2888 0.0715 0.0143 0.0023 0.0003 0.0000 0.0000
 0.1417-1.4448 0.6718 0.2002 0.0433 0.0072 0.0009 0.0001 0.0000 0.0000 0.0000
 5.2922
 0.1079-1.4544 0.6871 0.2197 0.0510 0.0090 0.0012 0.0001 0.0000 0.0000 0.0000
 -2.9264-1.7440 2.4121 0.9474 0.3232 0.0864 0.0185 0.0032 0.0004 0.0000 0.0000
 0.1079-1.4544 0.6871 0.2197 0.0510 0.0090 0.0012 0.0001 0.0000 0.0000 0.0000
 -2.9264-1.7440 2.4121 0.9474 0.3232 0.0864 0.0185 0.0032 0.0004 0.0000 0.0000
 0.1079-1.4544 0.6871 0.2197 0.0510 0.0090 0.0012 0.0001 0.0000 0.0000 0.0000
 5.5862
 0.0751-1.4647 0.6994 0.2376 0.0587 0.0110 0.0016 0.0002 0.0000 0.0000 0.0000
 -2.9776-1.7814 2.4102 0.9767 0.3550 0.1017 0.0232 0.0042 0.0006 0.0001 0.0000
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15.8765

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-4.0057-2.5448 2.2554 1.3296 0.8049 0.4903 0.2961 0.1748 0.0929 0.0412 0.0149
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16.1705

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-0.6081-1.7244 0.8093 0.4751 0.2750 0.1536 0.0750 0.0294 0.0091 0.0023 0.0005

16.4645

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 6.4960 0.0000 ARA1 (SUBSTRATE LATTICE VECTORS)
 0.0000 2.9580 ARA2
 12.9920 0.0000 ARB1 (OVERLAYER LATTICE
 VECTORS)
 0.0000 2.9580 ARB2
 1 IVECT (NUMBER OF
 INTERLAYER VECTORS)
 1.2650000 0.0000000 0.0000000 ASA(1,J),J=1,3

			NST1,NST1EFF,NTENS																					
			NLAY(i),i=1,NST1																					
			IFLAG																					
2	1	3																						
29	12																							
0																								
2	2																							
1	2	2	1	1	1	1	1	1	2	2	2	2	1	1	1	1	1	2	2	2	1	1	2	1
1	1	1																						
5	4	5	4	5	5	5	4	5	4	5	5													
0.0000	0.0000	0.0000																						
0.3560	-1.1539	1.4790																						
0.3560	1.1539	1.4790																						
0.5564	-2.5074	0.0000																						
0.5564	2.5074	0.0000																						
1.4490	5.5757	1.4790																						
1.4490	-5.5757	1.4790																						
1.7174	-1.4171	1.4790																						
1.7174	1.4171	1.4790																						
1.7634	3.0753	1.4790																						
1.7634	-3.0753	1.4790																						
2.1769	6.4960	0.0000																						
2.0414	0.0000	0.0000																						
3.5336	-3.0140	0.0000																						
3.5336	3.0140	0.0000																						
4.0154	0.0000	0.0000																						
4.1420	6.4960	0.0000																						
5.2938	2.3666	1.4790																						
5.2938	-2.3666	1.4790																						
5.1636	0.0000	1.4790																						
5.2590	-3.6009	0.0000																						
5.2590	3.6009	0.0000																						
5.5774	-4.1427	1.4790																						
5.5774	4.1427	1.4790																						
5.6226	6.4960	1.4790																						
6.0974	0.0000	0.0000																						
6.6088	6.4960	0.0000																						
7.2828	3.3321	0.0000																						
7.2828	-3.3321	0.0000																						
1.1604	0.0000	0.0000																						
0.50	0.00	-5.00																						
8.4432	1.2645	1.4790																						
8.4432	3.2480	1.4790																						
8.4432	-1.2645	1.4790																						

8.4432	0.0000	0.0000
9.7082	3.2480	0.0000
10.4262	0.0000	0.0000
11.6912	1.9830	1.4790
11.6912	3.2480	0.0000
11.6912	-1.9830	1.4790
11.6912	0.0000	1.4790
12.9562	0.0000	0.0000
13.6742	3.2480	0.0000
1.2650	0.0000	0.0000
0.50	0.00	-5.00
20.00	280.00	2.00

APPENDIX D

Support material for Carbon-Carbon Coupling of Formaldehyde on Reduced $\text{TiO}_2(110)$

S1 Additional figure illustrating the formation of diolate

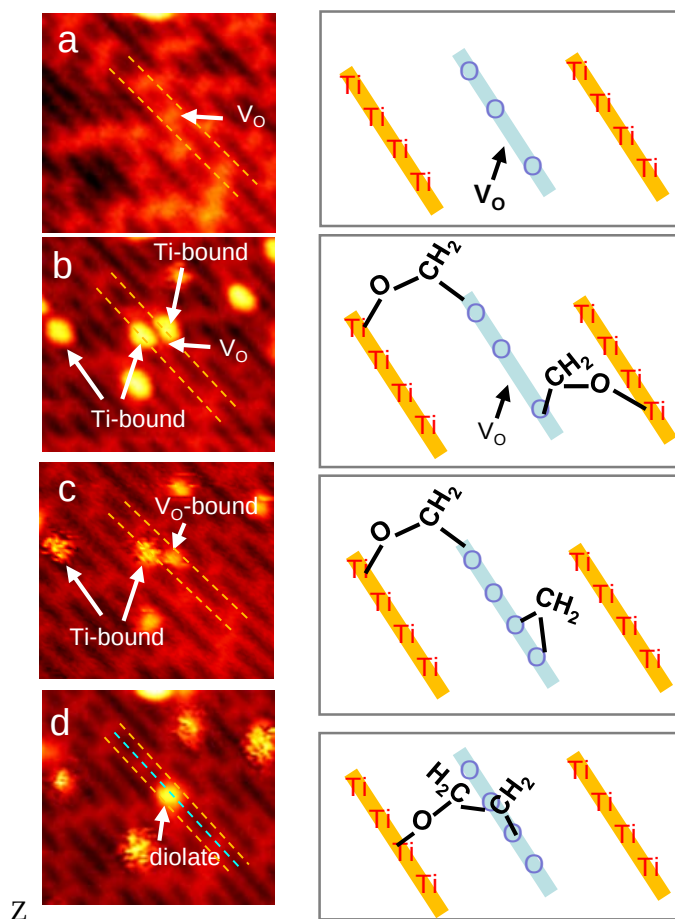


Figure S1. STM images obtained from the same area of reduced $\text{TiO}_2(110)$ at different temperatures, illustrating the formation of diolate via coupling of the Ti-bound formaldehyde and the V_O -bound formaldehyde: (a) clean surface imaged at 75 K, (b) surface imaged at 75 K after dosing 0.02 ML formaldehyde at 75 K ($V_b = 1.3$ V), (c) imaged at 145 K ($V_b = 1.5$ V) after

S2 The STM images showing the initial and the final status of sequence A.

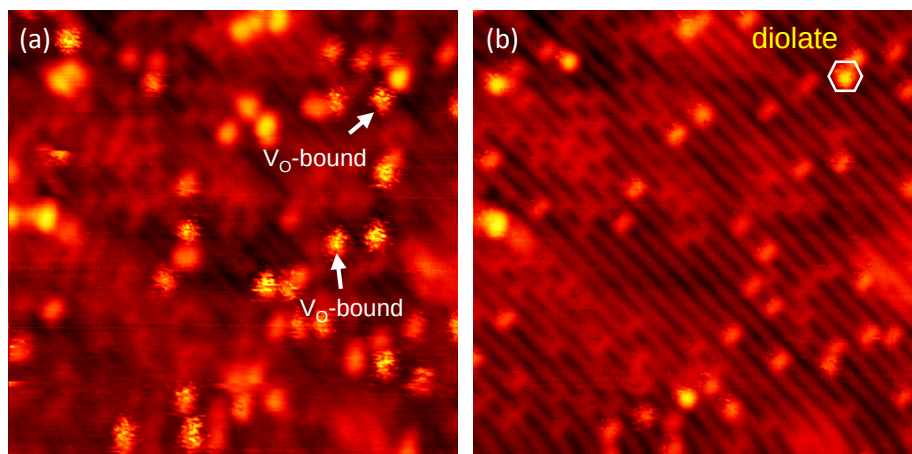


Figure S2. The isothermal STM images showing (a) the initial and (b) the final status of sequence A taken at 190 K.

S3 The images showing the initial and the final status of sequence B.

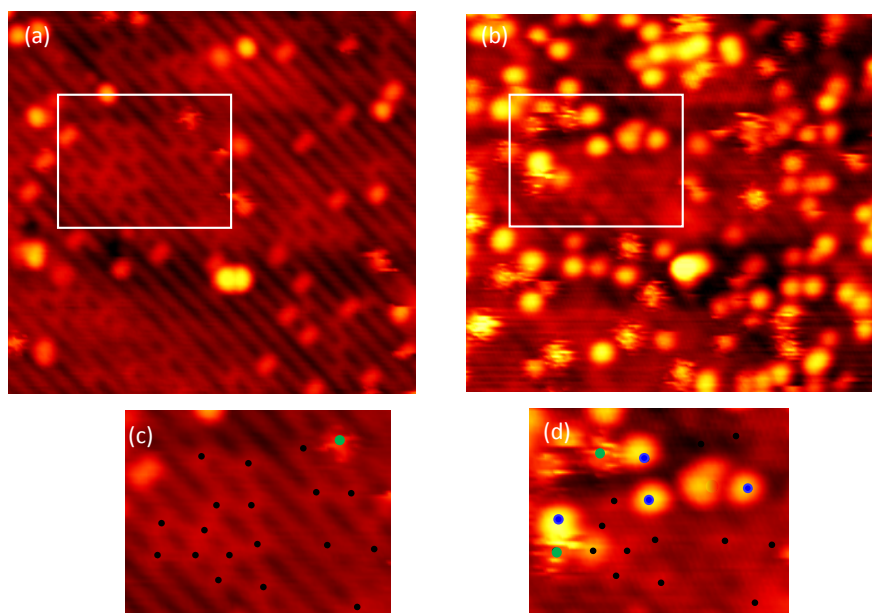
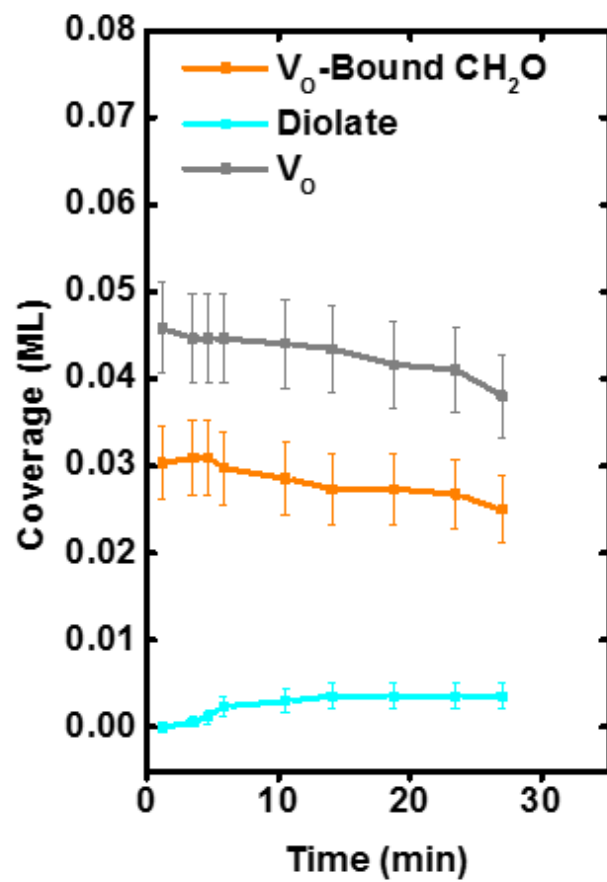


Figure S3. The isothermal STM images showing (a) the initial and (b) the final status of sequence B taken at 190 K. (c) and (d): Magnified areas marked in (a) and (b). Black dots mark the position of V_O 's. Blue dots and green dots mark the

S4 Another set of statistical analysis performed on the images of a surface at 180 K with less V_O -concentration (0.075 ML) to compliment Figure 3A.



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